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(b) (4), (b) (5)

BEST ORIGINAL COPY

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Original Submission

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7 April, 1978

Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, New York 10987

FAP 8B3394
J Smith

7 April, 1978

Petition for a Regulation, or Amendment to a Regulation,
for Fluorine Treated Polyethylene as sanctioned material
for use in producing, manufacturing, processing, preparing,
testing, packaging, transporting or holding foods.

(b) (5)



BEST ORIGINAL COPY

Prepared by:

R. S. Pender
UCC, SFRC

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7 April, 1978

Petitions Control Branch
Food and Drug Administration
Department of Health, Education & Welfare
Washington, D. C. 20204

Dear Sirs,

The undersigned, Union Carbide Corporation, submits this petition pursuant to Section 409(6)(1) of the Federal Food, Drug, and Cosmetic Act with respect to Fluorinated Polyethylene as food contact and/or storage items.

Attached hereto, in triplicate, and constituting a part of this petition are the following:

- A. Identity, composition and properties of indirect food additive.
- B. Amount of indirect food additive proposed for use.
- C. Intended physical or technical effect.
- D. Description of practicable extraction methods.
- E. Safety of indirect food additive.
- F. Proposed tolerance.
- G. Amendment.
- H. Environmental Impact Statement.

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SUMMARY

This report is a presentation of data and associated discussion of Union Carbide Corporation's current technology position in the area of polymer surface modification with fluorine gas. This instrument is specific to such modification by exposure of the polymer polyethylene, as a formed article, to gaseous fluorine under designated conditions of time and temperature to yield polymer with a less permeable surface. This unique property enhancement affords use of this so-changed polymer surface in application areas generally prohibitive for unmodified polyethylene. This is because of polyethylene's low barrier (high permeability) properties in the areas of use as food containers, especially where it contacts fats, oils, hydrocarbons, etc.

In the effort towards this petition, we've done substantial testing dealing primarily with discerning the nature and amount of extractables from the container into its contents, as it would be used in contact with food.

Data gathered to date, imply that while we improve properties, we minimally, if at all, alter the nature of these extractables from those of basic polyethylene under conditions of proposed use.

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INTRODUCTION

Union Carbide Corporation has developed a process wherein greatly improved barrier properties are imparted to processed (molded) polyethylene by exposure to fluorine gas at various concentrations in an inert gas, such as nitrogen, for varied treatment times and temperatures. This process as referred to in this petition, included such treatment on both polyethylene bottles that had been irradiated to improve mechanical properties for pressurized aerosol applications, and light weight-non irradiated polyethylene bottles for non pressure applications. However, such fluorination on film form polyethylene and other type containers and articles is also within the technology.

Basically we have a polymer substrate generally accepted for food and drug packaging applications on which only the surface character is changed to uniquely improve its utility. Such fluorinated surface layer is an integral part of the base polymer but leaves the polymer's bulk unaltered, i.e. still existing as polyethylene.¹

Because of this uniqueness, we sought to determine the appropriate regulation applicable to products materially modified similarly as fluorinated polyethylene for food contact applications.

An intensive search of Title 21-Food and Drugs of the Code of Federal Regulations yielded evidence of no situation specific to our product. Consequently we've performed numerous tests to determine the nature and amount of material extractable from our fluorinated polyethylene according to several Food and Drug Administration procedures for polyethylene, as well as some tests devised at Union Carbide to simulate extreme conditions of extraction. In addition, we've performed a series of tests according to FDA Guidelines for Indirect Food Additive Petitions.

From all the data presented here, we believe that the maximum levels of migrant, measured as ionic fluoride are at safe concentrations.

¹ See figures 1 and 2.

DISCUSSION

A. IDENTIFICATION OF MATERIALS

Polyethylene is an olefinic polymer of general structure $(H_2C:CH_2)_n$ and its general acceptance for use in application areas where it may contact food or drugs for human consumption is well established. Such general acceptance is acknowledged by specific citings in Food and Drug Administration (F&DA) Code of Federal Regulations such as, but not limited to, Title 21 sections 177.1520 and 175.300.

Fluorine is a nonmetallic halogen element of atomic number 9 and atomic weight 18.998. It exists, under conditions of our use, as a pale yellow diatomic gas (F_2) and is of pungent odor. Fluorine is the most electronegative element and is highly reactive forming fluorides with all elements except helium, neon and argon. The hazards of fluorine as a gas are its high toxicity and its activity as a strong corrosive irritant along with its flammability. Gaseous fluorine has a tolerance level of 1 p.p.m. in air¹ and is, with the existence of these cited properties, used and accepted in the manufacture of food and drug contact appliances and materials, e.g. fluorocarbon polymers.

The free fluorine gas is not an integral part of the articles resultant of our process but rather, because of its cited reactivity, exists as a fluoride chemically bonded to the polyethylene material. All excess "free gas" is removed from the process system prior to removing the treated articles for use and/or further processing, e.g. sterilization.

Nitrogen gas is the only other ingredient in this process of surface modification and is used as an inert diluent for the fluorine gas.

Typical concentrations for this gaseous treatment of polyethylene on a volume basis are (b) (4) for treatment of pressurized use containers and (b) (4) for non pressurized applications.

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¹ Condensed Chemical Dictionary - Ninth Edition, Van Norstrand/Reinhold

B. USAGE

1. The proposed usage of our fluorination process, where it pertains to food and drug end use applications, is to so modify containers and/or articles of polyethylene construction for single use applications, in contact with the following food types:

- a. Nonacid (pH above 5.0) aqueous products possibly containing salt and/or sugar, and including oil in water emulsions or low or high fat content
- b. Acidic (pH 5.0 or below) aqueous products possibly containing salt and/or sugar including oil in water emulsions of high or low fat content
- c. Aqueous acid or nonacid products containing free oil or fat possibly also containing salt and including water in oil emulsions of low or high fat content
- d. Dairy products and modifications
 - 1. Water in oil emulsion, high or low fat
 - 2. Oil in water emulsion, high or low fat
- e. Low moisture fats and oils
- f. Beverages - alcoholic and nonalcoholic
- g. Bakery products
- h. Dry solids

2. Maximum Temperature and Time of Storage for Packaged Food

This petition does not include a proposal for cooking food in the package described in this writing, but does include processing upon

packaging where such processing is a normal part of the manufacturing operation. Thus, the theorized maximum temperature would be that of high temperature sterilization, i.e. 250°F, during such processing. Time and temperature of normal storage is proposed to be that of duration of current, ordinary, competitive packaging materials for the markets of interest at temperatures ranging to theoretical maximum room temperature of 120°F.

3. Maximum Use Level of Additive and Maximum Thickness

In the strict sense of interpretation our process does not result in a coating as referenced in this category. Rather, as earlier stated, our fluorination process yields a moderate chemistry alteration on the surface of polyethylene as an integrally bound surface layer. This so-generated layer of fluorinated species affords the major barrier improvement to polyethylene even though this surface is of minimal thickness.

(b) (4)



4. Minimum Contents (Container Volume)

To respond to this point, we would currently propose no minimum container size except that limited by the dictates of practicality of the individual markets of use.

¹ Refer to Fig. 3

Included in the series of tests we've done were solvent extractions of containers of size 12 ounce capacity down to a 4 ounce volume. The smallest size (4 oz.) run in this series with the five solvents (deionized water, n-heptane, 50/50 ethanol-deionized water, 5/95 acetic acid-deionized water, and 50/50 ethanol-benzene) for 40 hour periods at reflux, yielded data, listed in Table I, showing fluoride¹ release level (measured as F⁻) to be well within what we believe to be safe limits in all cases (see Table II). The maximum level obtained in this extraction series was with water as the extracting agent, the values of fluoride ion measurable in the other extracting solvents were considerably lower. Therefore we restate our belief that if any criteria were established for minimum container size (surface/volume), they would have to follow the dictate of end use conditions, e.g. food type and processing conditions.

C. INTENDED PHYSICAL AND TECHNICAL EFFECTS

Polyethylene as it's normally manufactured for use has certain inherent limitations for food and drug applications. Among those limitations are its large permeability values to materials such as fluorocarbon and hydrocarbon propellents, aromatic and nonaromatic hydrocarbons, and fats and oils. These limitations prohibit the relatively inexpensive polyethylene polymer from use in many markets where its contents would be food and/or drugs.

Application areas, where these or similar materials are among the contents and polyethylene is otherwise desirable, are generally obliged to be satisfied by more expensive resins (e.g. polyethylene terephthalate), less aesthetically pleasing (e.g. metal cans) or less safe, breakable materials (e.g. glass). This is despite the fact that polyethylene is an accepted, FDA sanctioned material.

Union Carbide's fluorination process does much to overcome these limitations by creation of a thin surface layer that serves as an effective, permeation and solvent resistant barrier.

Data as included in Table 3 are typical of the kinds of permeation

¹ Fluoride release monitored by ion probe and neutron activation analyses as ppm fluoride ion concentration in solvent after extraction.

loss results we obtain on comparison of our fluorinated polyethylene versus nontreated polyethylene. In this table are listed data on permeation of various materials as contents of polyethylene containers. In each case containers of the same resin and size are compared, with the only difference being the presence of a fluorinated layer in the treated (non control) group. Among the chemical materials compared here as contents of the two container types are several used extensively in the food industry as flavoring agents as well as other chemical (nonfood) types. The data here show the polymer improvement by fluorination to be substantial.

Table IV of this section echoes this major improvement in the comparison data of treated and nontreated aerosol type polyethylene bottles with more expensive, competitive materials. Similar comparison data for non-aerosol applications are also presented in this table.

To date, no tests have been done with actual food items as contents of fluorinated containers. However, the data presented in these tables on some food components as well as other data including many extractant studies in food simulating and other solvents (presented in a later section) make it apparent that major improvement is afforded to polyethylene by our process of modification.

D. EXTRACTION METHODOLOGY

1. Among the extensive testing we've done on fluorinated polyethylene, extractions by a number of methods and solvents were included.

In the early phase of these studies, we at first attempted to establish a practical method of analysis and a range of extractable fluoride from bottles treated by our process. Data in Table I show the results of one such test wherein some fluorinated and control polyethylene bottles were extracted for a period of forty hours at reflux in solvents and solvent mixes. These results show that Neutron Activation Analysis, as used in the test, is not a sensitive enough analytical tool to accurately monitor the low levels of fluoride extracted from treated bottles. Essentially NAA could not distinguish between treated and nontreated

bottle extracts. You'll note in Table I also, that FLUORIDE ION probe measurements, which do show a distinction between the two extract types, show a maximum of 1.3 ppm fluoride ion despite the severity of the extraction conditions (all subsequent analyses are FLUORIDE ION probe). Even in this early stage, these data compare favorably with information on Table II, Fluoride Concentration Allowances. This list represents information from all sources we've gotten to date on acceptable fluoride concentration levels.

Tables V through VII are informational to show some of the kinds of things we've done in attempting to determine the maximum extractable fluoride and the technique for such extractions. Data in these tables show that, even when subjected to extraction conditions of impractical severity, our fluoride migration levels remain low.

In the progression to our most recent extraction tests, the prime object of this petition, some specific testing was done according to methods outlined in Title 21 of the Code of Federal Regulations. The methods were so chosen because of certain character similarities of our material to some materials for which regulations currently exist.

One such series was according to CFR-175.300 of Title 21 which is concerned with extractable residue from resinous coatings. Tables VIII through XI list some data gained of this testing. These tables clearly show that even though our material is not classed under this category, the residue extracted from the polymer easily meets the requirements for residue from polyethylene as food container coatings. It should be noted from these tables, that surface fluorination actually yields a reduction in extractable residue from the amount removed from nontreated (control) polyethylene. This result is significantly apparent in each case involving the solvents and conditions of CFR-175.300.

A modification of this regulation's requirements was our measurement of ionic fluoride removed from the containers during the extraction periods. Of significant importance from these fluoride ion measurements is that in cases involving all solvents of the required series,

except that involving 250°F water, concentration levels of less than 1ppm are measured. In the case involving the 250°F water extraction, a value of only 3.47ppm ionic fluoride is obtained. In all tests done to date this single value represents the highest we've been able to extract from our treated material under any conditions of temperature, duration, or solvent extraction.

Table XII lists data for similar extractions on containers for non-pressure applications. In this case, the treated bottle residue levels are generally higher than those for their irradiated aerosol counterparts, however, the numbers are still well within the regulated limits for polyethylene. Of major significance here though, is that the extractable fluoride ion values range only to a ppm level of 1.33 as a maximum for the 250°F water extraction from a minimum of 0.1 for the extraction in n-heptane.

Further testing in this intensive effort to determine the degree to which the extractable character of polyethylene is altered by our method of surface modification, involved a study according to CFR 177.1520. This regulation deals with olefin polymers as containers or components thereof as they might become additives from contact with food. This testing was done with our awareness that no statement of application to modified polyethylene was intended in this regulation. Specifications of this regulation, where it concerns polyethylene, call for refluxing separate samples for two (2) hours in the solvents hexane and xylene. The hexane extractable portion is measured as weight percent soluble portion in the boiling hexane of the original sample weight. According to the procedure this extracted amount should not exceed 5.5%. The xylene solubles are that portion remaining in solution at 25°C and should not exceed 11.3% of the original sample weight.

Table XIII shows the results of the study and it is apparent that we meet these criteria easily. Under the guidelines of this regulation no identification of the extractant is required. However infrared analysis of the xylene extracts from the polyethylene and fluorinated polyethylene samples show essentially the same material spectra, i.e. no IR detectable

fluorinated species is removed as a xylene soluble (see figures 4-6)

In addition to the aforementioned testing progressing to our most recent studies, we included examination of our material according to an existing regulation for perfluorocarbons. The regulation applicable to this completely fluorinated polymer, but not to our surface fluorinated polyethylene, is CFR 177.1550.

Our tests according to this regulation were purely investigational to establish comparison data to this FDA accepted fluorinated polymer.

Testing in the case of 177.1550 involved refluxing a given amount of material for 2 hour periods separately in the four solvents; distilled water, 50 percent ethanol and water, n-heptane, and ethyl acetate; with total extractives not to exceed 0.2 mg per square inch of material and total fluoride removed not to exceed 0.03 mg per square inch. The data in Table XIV show our partially fluorinated polyethylene to be strikingly close to meeting these criteria in the area of total extractables and to meet total removable fluoride limit. This is despite the fact that radically different processes are involved in the production of these two materials. We reiterate that we make no claim to having created a perfluorocarbon by our process but rather, we've made a technological advance in the area of surface character alteration.

The thrust of this writing is to petition for a new regulation or amendment of an existing regulation specifically dealing with Surface Fluorinated Polyethylene. To this end we've performed still additional extraction studies according to FDA Guidelines for Chemistry and Technology Requirements of Indirect Food Additive Petitions, March, 1976 edition.

In this phase of testing we used fluorinated containers of similar sizes and resins as used in the three immediately aforementioned studies (i.e. CFR 175.300, 177.1520, 177.1550) along with appropriate control containers. All samples were sterilized in each of their respective food simulating solvents (distilled water, 50% ethanol in water,

heptane, and 3% acetic acid) for the 2 hour period and at the ¹ temperatures suggested. Separate samples were monitored at the end of this period and then after 72 hours at reduced temperature². Intervals of 24 hours were used for further monitoring to a period of 168 hours. Selected time periods are those suggested in the FDA guidelines cited, except in the cases where n-heptane is the solvent where the minimum suggested times are exceeded, enhancing that extraction's severity.

In this, as in the other testing procedures we'd done previously, fluoride ion was the extractant monitored in the solvents.

The data in table XV are the average equilibrium values of fluoride ion extractant at the time periods specified.

It should be noted in this table, that the extractable fluoride values listed when n-heptane is the extracting solvent are not divided by five (5) as suggested but are the actual average values found.

Examination of these data shows that most values for extractable fluoride in all solvents are essentially 1ppm or less. The exceptions are with the irradiated-fluorinated aerosol type containers where water, 50% ethanol in water, or 3% acetic acid is used as the solvent. In this case, a maximum equilibrium value of approximately 2.3ppm is yielded with distilled water as the solvent.

Further examination of this table shows that equilibrium extracted fluoride for all samples is reached by 72 hours. It should also be noted, from this table, that n-heptane is the solvent extracting the minimum amount of fluoride ion.

Complete data for these tests are presented in tables XVI through XXIII. In these tables, of significance is the observation that the solvents extracting the largest fluoride amounts, (>1ppm) cited earlier, extract nearly their equilibrium values during the sterilization periods.

¹ Sterilization temperatures: Water-250°F, Acetic Acid-212°F, Ethanol/Water-160°F, Heptane-150°F

² Equilibrium temperature: All solvents-120°F

It is acknowledged that among these data are extractable fluoride concentration levels above the 1 ppm level cited in table II for the fluoride concentration allowance in potable water. In that same table is listed the large, American Dental Association accepted, level of 1000 ppm available fluoride ion for inclusion in toothpastes. This high level is the commonly included concentration in most commercial brands. With toothpastes being a commodity item used several times per day almost universally for the lifetimes of individuals, our maximum extracted level of fluoride of 2.3 ppm, by food simulating solvents, appears minor. We hold this position because it's unreasonable to assume that the degree of commercial acceptance or need for our proposed single use fluorinated polyethylene container would even remotely approach the universality of fluoride incorporated toothpaste.

If, however we were to assume a 100% market penetration and all food consumed by humans were from fluorinated polyethylene containers and we were in addition to take our worst case, that of aqueous, sterilized foods, and assumed further that the average 1500 gm/day diet were totally aqueous, then the maximum daily consumption of fluoride as an indirect food additive would be approximately 31 ppm per day.

If, however we were to divide the average daily diet into its standard proportions of 133 gm fatty food and 683.5 gm each of aqueous and acidic food components, we would have a dramatically different picture. Assuming again, exclusive usage of our containers for a 1500 gram per day diet, with component division, the amount of fluoride consumed would be on the order of 7.0 ppm. Both the above stated figures are based on the maximum extractable fluoride by each of the appropriate solvents and are for the containers used in this study which have an approximate internal surface area of 37.986 inches square.

Again, even at these theoretical 100% market penetration levels, the available fluoride amount is relatively small, especially when compared to the non-theoretical, but actual, toothpaste concentration.*

It would appear obvious that markets of interest do not incorporate

* Refer to Appendix, Table I.

all normal food applications. A contention on our part of 10% of all packaged consumer food items would be contained in fluorinated polyethylene is probably more reasonable, but is nonetheless presumptuous. However if we were able to gain that degree of penetration, the consumed fluoride levels would then decline to 3.1 ppm for a totally aqueous diet and 0.70 ppm for the average diversified diet.

To determine the nature of the removed fluoride and other extractables, chemical analysis of the residue from the water sterilization was done by an independent laboratory. This analysis showed that all (total) fluoride removed from the treated polymer is ionic, i.e. no detectable polymerically bound fluoride is removed.¹ Other material coming off during this extraction process is believed to be essentially fragmented polyethylene as is normal with this polymer. That is, the analysis showed other materials present to be carbon, hydrogen and some traces of nitrogen.

2. Analytical Methodology

The analytical method used predominantly to obtain the fluoride ion concentration values reported in this petition, involved potentiometric determination using an ion probe specific for fluorine. A complete description of this method is included as Appendix 1.

Other fluoride analyses were done by an outside, independent analytical service organization.¹

Used in all of the extraction studies described in this document, were samples as bottles containing their volume of the respective solvents. As such, the analyses were done on volumes of fluoride solutions equivalent to the container's capacity. Consequently, all numbers of fluoride concentration as found are in terms of container contents.

To validate the reliability of the tests performed and the analytical methods thereof, samples of known concentrations of fluoride ion in water were run via two methods.

In the first case, we wished to monitor the extent of fluoride migration, during the extractions, into any glass which may be a part of

¹ Schwarzkopf Microanalytical Laboratories, 56-19 37th Ave., Woodside, N.Y. 11377

the extraction apparatus. This information was necessary, we felt, for instances where the samples may have plastic pieces as non-containers and glass kettles are used as the containing vessel for the solvent and the fluorinated polyethylene pieces. In this study, hydrofluoric acid was added in four concentration levels to water. The fluoride concentrations of these solutions were measured by ion probe titration then the samples were refluxed. At the end of a forty (40) hour period, the solutions were cooled and again monitored for fluoride ion concentration. The results of this study are shown in Table XXIV and reveal that the fluoride ion concentration does diminish during the act of refluxing in contact with glass and the fluoride source is hydrofluoric acid. It should be stated here that in the extraction tests as described earlier in this writing, the samples were plastic bottles of the type for which the petition is submitted with the extracting solvents contained therein.

The second effort to determine ion probe analytical reliability and ionic fluoride maintenance ability during the extraction period involved placing known concentrations of ionic fluoride in some aerosol and non-aerosol plastic containers (non-fluorinated) of the type used in this study overall. Some similar sized glass containers were also filled with known concentrations of the same fluoride solution and included in this study. The fluoride source in this study was sodium fluoride. All samples were analyzed before and after sterilizing in water at 250°F for 2 hours and allowing equilibrium extraction at 120°F to 168 hours.

The data from this investigation are presented in Table XXV and show no detectable loss in any of the samples tested by this method.

E. SAFETY OF THE FOOD ADDITIVE

(See Section A - Identity of Food Additives - Fluorine)

Even though the airborne and skin contact tolerance of gaseous fluorine is but a few ppm, many of its fluorides for the most part are apparently considered much less dangerous. This is made obvious by the generally sanctioned, widespread usage in national and municipal programs where fluorides are deliberately added to water for human ingestion. Further support of this belief is gained by the high level accepted by the ADA for continual

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oral ingestion via toothpaste and other dentifrice incorporation. These and other data as listed in Table II are generally in or exceeding the range of fluoride extractable as a result of our treatment on polyethylene. The relatively low maximum levels of fluoride we were able to extract from our fluorinated polyethylene, even under the most severe conditions of extraction, we feel, place us well within safe limits if we are to judge data from this table as valid criteria for safe limits. A Division of Toxicology review of these levels of fluoride should determine if these common use allowances are within safe limits.

F-G PROPOSED TOLERANCE

To propose a tolerance level for extractable fluoride from fluorine treated polyethylene we'd have to follow the guidelines of currently allowable limits of fluoride in consumable articles. Even with the exclusion of the high ADA fluoride acceptance level (1000ppm F^-) the extractable level of fluoride from fluorinated polyethylene is generally within the range of the other listed concentration allowances in Table II. Where we venture outside this range, we do so only minimally and only in the cases involving distilled water at 250°F and ethanol/water at 212°F. In these cases we achieve a high value of ~ 2 ppm F^- , a value only slightly outside the lowest levels of the allowance limits listed in Table II. Considering once again the projected limited consumption of food items from containers produced of this technology, (see pages 12-13) a relative small effect, if any, from this allowance level would result. Taking into account the high levels of fluoride taken in in the normal course of oral hygiene, per individual per day, it's suggested that no adverse effect would be felt from these amounts.

We do not propose unlimited allowable fluoride extractive nor even the 1000ppm F^- accepted value for oral hygiene items. but rather limitations commensurate with good manufacturing processes. It's neither to our advantage nor is it our desire to include in our process technique, amounts of fluorine in the treatment greatly in excess of that needed to achieve the intended technical effect. That effect is to create barrier properties on polymers. In the same vein, allowing such loose parametric control of our

process so as to yield excessive extractants as fluoride and or residue would be counterproductive.

With this in mind we would propose a regulation and/or amendment to read somewhat as follows:

Fluorinated Polyethylene - where polyethylene articles are surface modified by action of fluorine gas in combination with other gases as inert diluents with such action leaving the polymer's bulk unchanged. Fluorine gas shall be used in concentrations not in excess of amounts necessary to achieve the intended technical effect in the food or drug contact article and yielding extractable residue not in excess of that of basic polyethylene when extracted by food simulating solvents under the prescribed conditions (e.g. conditions of 177.1520 and 175.300) and not to have extracted from its surface fluoride ion in excess of 5ppm based on container contents.

H. ENVIRONMENTAL IMPACT ANALYSIS

No environmental impact study has been made as such. However it would seem likely that no impact greater than ordinary for single use containers would result from use of containers of fluorinated polyethylene. This position is advanced in that no greater technology would be involved in disposal of this so produced container than other polymeric single use containers. That is, fluorinated polyethylene should be amenable to all normal disposal routes as ordinary polyethylene such as regrinding, land fill use, fuel (energy) recovery, etc.

The process of manufacturing fluorinated polyethylene involves formed articles (film, bottles, etc.) of polyethylene and exposing them to fluorine gas mixed with an inert diluent gas of various concentrations for specified times and at specified temperatures. All fluorine gas and other gases used in our process of said production, are handled and transferred in a closed system. This is inclusive of all gaseous by-products. The current design of our system is of such efficiency that only a small percentage of the reactive gas mix is used per treatment. (b) (4)

(b) (4)



Thus it's our belief that the adverse environmental impact of the process would be nil or minimal, having no free fluorine loosed to the atmosphere and no other deleterious gases evolved to human exposure conditions. In addition, the fact that waste is transformed to an easily handled condition without manual manipulation and before removal from the system supports this position.

Tables

Table I

Extraction Results on Fluorinated 4-oz. Rainville
Aerosols and Controls Refluxed for 40 Hours

<u>Solution</u>	Parts per Million (a)			
	<u>N.A.A.</u> Control	<u>N.A.A.**</u> Treated	<u>F⁻ electrode</u> Control	<u>F⁻ electrode**</u> Treated
Deionized Water	(b) (4)			
n-Heptane				
50/50 ETOH/D.I. Water				
5/95 Acetic Acid/D.I. Water				
50/50 ETOH/Benzene				

(a) Values based on bottle contents.

** Treated (b) (4)

For discussion of this table see pages 6, 7, 8.

Table II

FLUORIDE CONCENTRATION ALLOWANCES

<u>Source</u>	<u>Concentration</u>	<u>Detected As</u>
Threshold Limit Value ¹ (TLV)	3 ppm	HF
Home and Industrial Water Fluoridation Level	1 ppm	F ⁻
Bottled Water Level (Potable)	1 ppm	F ⁻
FDA- 177.1550 Section 21 Extractable Fluoride from Perfluorocarbons	1.3 ppm ²	F ⁻
OSHA Airborne Tolerance Level	1 ppm	F ₂
American Dental Assoc. Accepted Level (Toothpaste)	1000 ppm	F ⁻

¹ Threshold Limit Value (TLV) - Atmosphere concentration level sufficient to cause skin irritation.

² 1.3 ppm based on use of bottle of 236.8 cc interior volume.

For discussion of this table see pages 6, 12, 15.

Table III

PERMEATION DATA FOR VARIOUS MATERIALS
As Contents of Fluorinated and Control
Polyethylene Bottles

<u>BOTTLES</u>	<u>CONTENTS</u>	<u>TRTMT NUMBER</u>	<u>TEST TEMP</u>	<u>TIME ON TEST</u>	<u>LOSSES %</u>	
					<u>CONTROL</u>	<u>TREATED</u>
Wheaton LDPE	Hexane	1	Ambient	3 months	(b) (4)	
"	"	1	120°F	3 months		
"	Xylene	1	Ambient	3 months		
"	"	1	120°F	3 months		
Wheaton HDPE	Hexane	1	Ambient	3 months		
"	"	1	120°F	3 months		
"	Xylene	1	Ambient	3 months		
"	"	1	120°F	3 months		
Consupak 8 oz HDPE	Octyl Acetate	2	120°F	1 month		
"	n-Butyl Acetate	2	120°F	1 month		
"	Butyl/Benzoate	2	120°F	1 month		
"	Menthol	2	120°F	1 month		
"	Amyl Acetate	2	120°F	1 month		
Irradiated 8 oz Captive HDPE Aerosol	30/70 Ucon 12/11	3	130°F	1 month		
"	Butane	3	130°F	1 month		
"	A-46	3	130°F	1 month		

TREATMENTS:

#1 -
#2 -
#3 -

* Failed = Lost all contents.

For discussion of this table see page 6.

Table IV

COMPARISON PERMEATION DATA OF FLUORINATED AND
NON-FLUORINATED POLYETHYLENE TO COMPETITIVE BARRIER MATERIALS

- PRESSURIZED APPLICATIONS -				LOSS
<u>CONTAINER MATERIAL</u>	<u>PERMEANT</u>	<u>TEMPERATURE</u>	<u>TEST TIME</u>	(b) (4)
Non-fluorinated HDPE*	Low Pressure Fluorocarbon Mixture	130°F	1 month	
"	High Pressure Fluorocarbon Mixture	130°F	1 month	
Fluorinated HDPE*	Low Pressure Fluorocarbon Mixture	130°F	1 month	
"	High Pressure Fluorocarbon Mixture	130°F	1 month	
Celcon**	Low Pressure Fluorocarbon Mixture	130°F	1 month	
"	High Pressure Fluorocarbon Mixture	130°F	1 month	
Valox***	Low Pressure Fluorocarbon Mixture	130°F	1 month	
"	High Pressure Fluorocarbon Mixture	130°F	1 month	
- NON-PRESSURIZED APPLICATIONS -				
Oriented Polypropylene	Hexane	Ambient	1 month	
" "	Xylene	Ambient	1 month	
Propylene	Hexane	Ambient	1 month	
"	Xylene	Ambient	1 month	
Polyvinyl Chloride	Hexane	Ambient	1 month	
" "	Xylene	Ambient	1 month	
Fluorinated HDPE	Hexane	Ambient	1 month	
" "	Xylene	Ambient	1 month	

* HDPE = High Density Polyethylene

** Celcon = Trademark for copolymerized acetal resin

*** Valox = Polybutylene Terephthalate

For discussion of this table see page 7.

Table V

40 Hour Refluxing of Deionized Water
on 8-oz. Consupak Bottles for Extractables
Measured by F⁻ Probe

<u>Sample</u>	<u>Parts Per Million Fluoride</u> ^(a)
Control Bottle	(b) (4)
(b) (4)	
Deionized Water	

(a) Values based on bottle contents.
* (b) (4)

000027

Table VI

40 Hour Reflux Extractions of Treated, Then Cut Up
8-oz. Consupak Bottles (b) (4), Using Various Solvents
Measured by F⁻ Probe

<u>Solvent</u>	<u>Parts Per Million Fluoride</u> ^(a)
n-Heptane	(b) (4)
50/50 ETOH/Deionized Water	
5/95 Acetic Acid/Deionized Water	
8/92 ETOH/Deionized Water	
Deionized Water	

(a) Values based on bottle contents.

*

(b) (4)

For discussion of this table see page 8.

Table VII

40 Hour Refluxing of 8% ETOH Solutions On
8-oz. Consupak Bottles Using Varying Techniques for Extractables
Measured by F⁻ Probe

<u>Sample</u>	<u>Parts Per Million Fluoride</u> (a)
Fluorinated* first, many small pieces	(b) (4)
Many small pieces first, then fluorinated*	
Fluorinated* first, few large pieces	
Cut up, non-fluorinated	

(a) Values based on bottle contents.

* (b) (4)

For discussion of this table see page 8.

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Table VIII

Extractions of Treated* Aerosol Bottles
Using Deionized Water at 250°F for 2 Hours

	<u>Residue in p.p.m.</u> ^(a)	<u>Free Fluoride Ion in p.p.m.</u> ^(a) Measured by F ⁻ Probe
Control	<div>(b) (4)</div>	
Irradiated Only		
Irradiated First, Then Fluorinated		
Fluorinated Only		
Fluorinated First, Then Irradiated		

Note: According to FDA procedures, < 50 ppm is an acceptable figure for polyethylene residue.

(a) Values based on bottle contents.

(b) (4)

** Average of three samples.

For discussion of this table see pages 8, 9.

Table IX

*
Extractions of Treated Aerosol Bottles
Using 5% Acetic Acid Solution at 150°F for 2 Hours

	<u>Residue in p.p.m.</u>	<u>Free Fluoride Ion in p.p.m.</u> ^(a) Measured by F ⁻ Probe
Control	(b) (4)	
Irradiated Only		
Irradiated First, Then Fluorinated		
Fluorinated Only		
Fluorinated First, Then Irradiated		

Note: According to FDA procedures, < 50 ppm is an acceptable figure for polyethylene residue.

(a) Values based on bottle contents.

(b) (4)

** Average of three samples

= No Detection

For discussion of this table see pages 8, 9.

Table X

EXTRACTION OF TREATED AEROSOL BOTTLES
USING 8% ETHANOL SOLUTION AT 150°F FOR 2 HOURS

<u>Residue in p.p.m.¹</u>	<u>Free Fluoride Ion in p.p.m.^{1*}</u> Measured by F ⁻ Probe
--------------------------------------	---

Control

Irradiated Only

Irradiated first, then fluorinated

Fluorinated Only

Fluorinated first, then irradiated

(b) (4)

Residue: < 50 ppm is an acceptable value for polyethylene residue according to FDA procedures.

¹ Values based on bottle contents.

* Average of three samples.

(b) (4)

For discussion of this table see page 8, 9.

Table XI

EXTRACTION OF TREATED AEROSOL BOTTLES.
USING n-HEPTANE AT 150°F FOR 2 HOURS

<u>Residue in p.p.m.¹</u>	<u>Free Fluoride Ion in p.p.m.^{1*}</u> Measured by F ⁻ Probe
--------------------------------------	---

Control

Irradiated Only

Irradiated first, then fluorinated

Fluorinated Only

Fluorinated first, then irradiated

(b) (4)

Residue: < 50 ppm is an acceptable value for polyethylene residue according to FDA procedures.

¹ Values based on bottle contents.

* Average of three samples

(b) (4)

ND = none detectable

For discussion of this table see pages 8, 9.

000033

TABLE XII

SOLVENT EXTRACTION PER FDA 175.300Residue and F⁻ Determination for 8-oz. Non-Aerosol Polyethylene Bottles

<u>Solvent</u>	<u>Temp.</u> <u>°F</u>	<u>Duration</u>	<u>Control</u>		<u>F₂ Treated¹</u>	
			<u>F⁻</u>	<u>Residue</u> (ppm)	<u>F⁻</u>	<u>Residue</u> (ppm)
Deionized Water	250	2 Hours	(b) (4)			
Deionized Water	212	30 Minutes				
Deionized Water	150	2 Hours				
8% ETOH Solution	150	2 Hours				
5% Acetic Acid Solution	150	2 Hours				
n-Heptane	150	2 Hours				

For discussion of this table see page 9.

(b) (4)

000034

TABLE XIII

HEXANE AND XYLENE

EXTRACTABLES FROM POLYETHYLENE ACCORDING TO CRF-177.1520

<u>CONTAINER</u>	<u>HEXANE*</u> <u>SOLUBLES (%)</u>	<u>XYLENE**</u> <u>SOLUBLES (%)</u>
Control High Density Polyethylene [†] Aerosol Type	(b) (4)	
Fluorinated ¹ /Irradiated HDPE [†] Aerosol Type		
Fluorinated ¹ /Irradiated ² HDPE Aerosol Type		
Irradiated ³ HDPE Aerosol Type		
Irradiated ³ /Fluorinated ¹ HDPE Aerosol Type		
Irradiated ² HDPE Aerosol Type		
Irradiated ² /Fluorinated ¹ HDPE Aerosol Type	(b) (4)	

For discussion of this table see page 9.

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Table XIV

Solvent Extraction Per FDA 177.1550

<u>Sample</u>	<u>Residue *</u>	<u>mgF⁻/in²**</u>
8-oz. Non-Aerosol Control	(b) (4)	
8-oz. Non-Aerosol - F ₂ Treated ¹		
8-oz. Irradiated Aerosol (Control)		
8-oz. Irradiated/Fluorinated Aerosol ²		

(b) (4)

For discussion of this table see page 10.

TABLE XV

EQUILIBRIUM FLUORIDE CONCENTRATIONS FROM ¹FOOD
SIMULATING SOLVENT EXTRACTIONS OF FLUORINATED POLYETHYLENE
(All ppm F⁻ values based on bottle contents)

<u>SOLVENT</u>	<u>EQUILIBRIUM</u> <u>F⁻ CONCENTRATION (ppm)</u> <u>Measured by F⁻ Probe</u>				<u>TIME TO</u> <u>EQUILIBRIUM</u>
	<u>Bottle Type</u>				
	² Control	³ Fluorinated	Control	Fluorinated ⁴	
	<u>non-aerosol</u>	<u>non-aerosol</u>	<u>aerosol</u>	<u>aerosol</u>	
⁵ Distilled Water	(b) (4)				72 hrs.
50% Ethanol/Water					72 hrs.
3% Acetic Acid					72 hrs.
⁶ N-Heptane					72 hrs.

- ¹ Samples sterilized 2 hrs. - Distilled water in container @ 250°F/2 hrs.
- 50% ethanol/water in container @ 160°F/2 hrs.
- 3% acetic acid in containers @ 212°F/2hrs.
- Heptane in containers @ 150°F/2hrs.

After sterilization all temperatures are reduced to 120°F for duration of test.

- ² All samples used in this test are 8 oz. polyethylene bottles of two wall thicknesses and shapes, both however are of ~37.99 inches square internal

(b) (4)

For discussion of this table see pages 10, 11.

000037

Table XVI

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Thin Walled Captive - Non Aerosol

SOLVENT: Distilled H₂O

MEASURED EXTRACTANT: Fluoride Ion (F⁻) - Measured by F⁻ Probe

TIME ON TEST	PPM F ⁻		PPM F ⁻	
	CONTROL	FLUORINATED	Post NaOH wash extraction CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				
168 hrs.				
168 hrs.				

* ND = None Detectable (≤ 0.025 ppm F⁻)

Table XVII

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Irradiated Aerosol

SOLVENT: Distilled H₂O

MEASURED EXTRACTANT: Fluoride Ion (F⁻) - Measured by F⁻ Probe

TIME ON TEST	PPM F ⁻		Post NaOH wash extraction	
	CONTROL	FLUORINATED	CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				
168 hrs.				
168 hrs				

* ND = None Detectable (≤ 0.025 ppm F⁻)

For discussion of this table see pages 10, 11.

Table XVIII

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Thin Walled Captive - Non Aerosol

SOLVENT: 3% Acetic Acid

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		Post NaOH wash extraction	
	CONTROL	FLUORINATED	CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				

*ND = None Detectable (≤ 0.05 ppm F^-)

For discussion of this table see pages 10, 11.

000040

Table XIX

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Irradiated Captive Aerosol

SOLVENT: 3% Acetic Acid

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		PPM F^-		PPM F^-
	CONTROL	FLUORINATED	Post NaOH wash extraction CONTROL	FLUORINATED	212°F steriliz- ation -
Sterilization only	(b) (4)				
Sterilization only					
72 hrs.					
72 hrs.					
96 hrs.					
96 hrs.					
120 hrs.					
120 hrs.					
144 hrs.					
144 hrs.					
168 hrs.					
168 hrs.					

*ND = None Detectable (≤ 0.05 ppm F^-)

For discussion of this table see pages 10, 11.

Table XX

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Thin Walled Captive - Non Aerosol

SOLVENT: 50% Ethanol/Water

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		PPM F^-	
	CONTROL	FLUORINATED	Post NaOH wash extraction CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				
168 hrs.				
168 hrs.				

*ND = None Detectable (≤ 0.025 ppm F^-)

Table XXI

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Irradiated Aerosols

SOLVENT: 50% Ethanol/Water

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		Post NaOH wash extraction	
	CONTROL	FLUORINATED	CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				
168 hrs.				
168 hrs.				

*ND - None Detectable (≤ 0.025 ppm F^-)

For discussion of this table see pages 10,11.

Table XXII

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Thin Walled Captive - Non Aerosol

SOLVENT: Heptane

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		PPM F^-	
	CONTROL	FLUORINATED	Post NaOH wash extraction CONTROL	FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				

*ND = None Detectable (≤ 0.01 ppm F^-)

For discussion of this table see pages 10, 11.

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Table XIII

SOLVENT EXTRACTION STUDIES FOR DETERMINATION OF COMPLIANCE WITH
"REQUIREMENTS OF INDIRECT FOOD ADDITIVES"

SAMPLE TYPE: Irradiated Aerosols

SOLVENT: Heptane

MEASURED EXTRACTANT: Fluoride Ion (F^-) - Measured by F^- Probe

TIME ON TEST	PPM F^-		PPM F^-	
	CONTROL	FLUORINATED	Post NaOH wash CONTROL	extraction FLUORINATED
Sterilization only	(b) (4)			
Sterilization only				
72 hrs.				
72 hrs.				
96 hrs.				
96 hrs.				
120 hrs.				
120 hrs.				
144 hrs.				
144 hrs.				
168 hrs.				
168 hrs.				

* ND = None Detectable (≤ 0.01 ppm F^-)

For Discussion of this Table, see Pages 10, 11

Table XXIV

40 Hour Reflux of Hydrofluoric Acid Solutions in Glass Kettles
To Check Migration of Fluoride Into Glass Wall

Calculated and measured parts per million using the F⁻ ion electrode.

<u>Sample</u>	<u>Calculated</u>	<u>F⁻ Ion Electrode</u>		<u>%Δ</u>
		<u>Before Boiling</u>	<u>After Boiling</u>	
A	(b) (4)			
B				
C				
D				
Deionized Water				

For Discussion of this Table, see Pages 13, 14

Table XXV

EFFICIENCY STUDY
OF
FLUORIDE ION LOST DURING EXTRACTION
Measured by F⁻ Probe

<u>SAMPLE ID</u>	<u>CONTENTS</u>	<u>CONTAINER TYPE</u>	<u>TIME ON TEST</u>	<u>PPM F⁻</u>
(b) (4)				

All samples are solutions in distilled water.
Conditions for study are 250°F/2hrs, then 120°F for all additional time.

For Discussion of this Table, see Page 14

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Figures

(b) (4)

Transmission Infra Red Spectrum
of Fluorinated High Density Polyethylene
[Reference Spectrum/of Non-Treated HDPE Film in Appendix Figure 1]
(For discussion of this figure see page 5)

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(b) (4)

Surface (ATR) Infra Red Spectrum of
Fluorinated High Density Polyethylene Film

(For discussion of this figure see page 5)

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(b) (4)



Typical SEM picture of non-fluorinated polyethylene (NOTE: absence of treatment layer).

Typical SEM picture of fluorinated polyethylene film showing distinct treated surface layer.

Scanning Electron Microscope Photographs
(for discussion of this figure, see Page 5)

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(b) (4)



Infra Red Spectrum of
Xylene Extract from Low Density Polyethylene
(b) (4)

(For discussion of this figure see page 9)

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(b) (4)

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Infra Red Spectrum of
Xylene Extract from Irradiated High Density Polyethylene

(b) [REDACTED]

(For discussion of this figure see page 9)

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(b) (4)

Infra Red Spectrum of
Xylene Extract from Irradiated-Fluorinated High Density Polyethylene
(b) (4)

(For discussion of this figure see page 9)

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Appendix

APPENDIX 1

Analytical - (Ref. Page

Following is a reprint of the general procedure for potentiometric fluoride analysis as published by the manufacturer of the analytical equipment used.

Specific to our types of analyses, however, the procedure as outlined below is used:

Basic Analysis:

Samples are diluted, 1:1, with TISAB¹ and the electrical potential is measured. The F^- value is then obtained by comparison to a standard curve prepared from solutions of NaF in deionized water which were diluted with TISAB¹ and run in the same manner as the samples.

Standards Preparation:

1. Samples in Dilute Acetic Acid Solution. Standards are made up to contain similar amounts of acetic acid as the samples.
2. Samples in Ethanol. Standards are made up to contain similar amounts of ethanol as the samples.
3. Samples in 0.1 N or More Dilute Caustic (NaOH or KOH). Standards are made up to contain similar amounts of caustic as the samples. The pH of the solution is checked after mixing with TISAB¹ and if not between 5-7 either more of the buffer¹ is needed or the same buffer to which acetic acid has been added.
 - (a) Samples with Caustic Concentration >0.1 N. These samples need to be either diluted or neutralized before proceeding. Appropriate standards are then run.

¹TISAB® - Trademark for Orion Corporation's Total Ionic Strength Buffer.

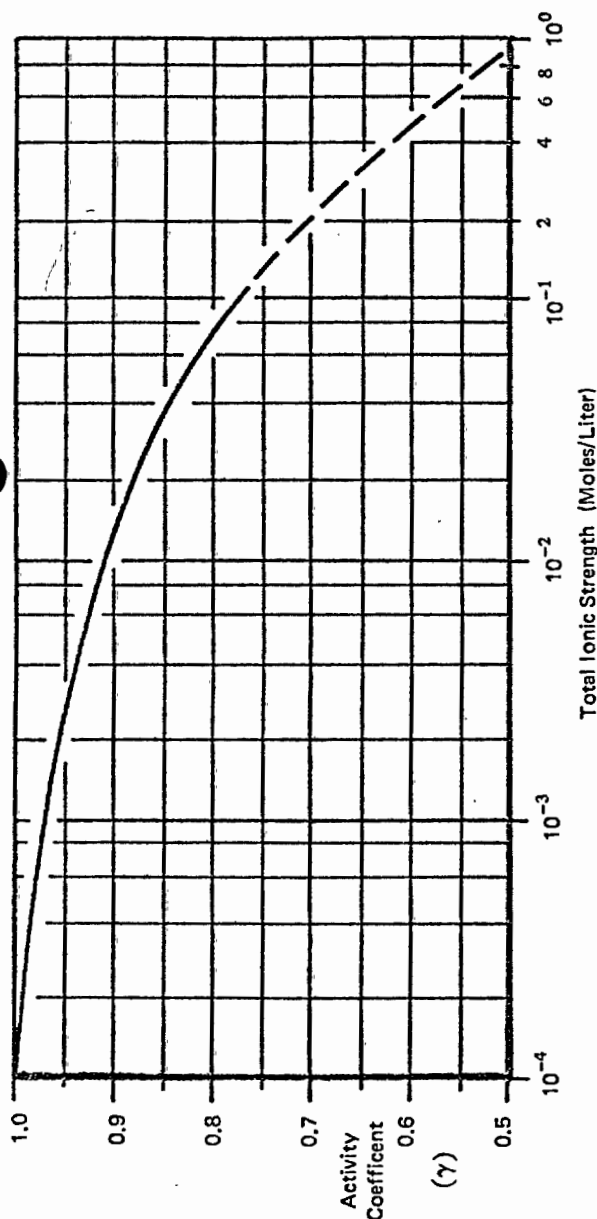
- (b) Samples High in F⁻ Concentration. Samples should be neutralized then titiated with La(NO₃)₆ solution (described in the following reprint).

4. Samples in Hexane or Other Hydrocarbon.

- (a) Evaporated samples in presence of known amount of caustic (e.g., 5 ml of 0.1 N) until all organic solvent has evolved. Dilute remaining material and proceed as above for 0.1 N caustic samples. For standards, evaporate so prepared standards in the same manner and run similarly as samples.
- (b) An alternate method to (a) (above) is to extract volumes of samples with 0.1 N caustic and run as for previously described 0.1 N caustic samples. Standards for 0.1 N caustic should, in this case, be shaken with same organic present in samples and run.

figure 1

Ionic activity coefficient of fluoride as a function of total ionic strength. Data below 10^{-1} M are calculated from the Debye-Hückel theory, using the values of Kielland, *J.A.C.S.*, 59, 1675 (1937). The values between 10^{-1} M and 1 M are estimated from electrode measurements.



chemistry of fluoride ion

The total fluoride concentration is given by the following equation:

$$1) \quad C_t = C_f + C_b$$

where: C_t = total fluoride concentration
 C_f = free fluoride concentration
 C_b = concentration of bound and complexed fluoride

The following relationship exists between the free fluoride ion concentration and the fluoride ion activity:

$$2) \quad A = \gamma C_f$$

where: A = fluoride ion activity
 γ = fluoride ion activity coefficient
 C_f = free fluoride ion concentration

The fluoride activity coefficient (γ) depends on the solution total ionic strength. Figure 1, shows the activity coefficient for fluoride ion as a function of total ionic strength. If the approximate sample composition is known, the total ionic strength can be estimated as shown in Appendix I.

effect of hydrogen ion

In acid solutions, hydrogen ion forms complexes with fluoride ion, such as the undissociated acid HF and the ion HF_2^- . Figure 2 shows the proportion of free fluoride ion in acid solutions. Note that hydrogen complexing is negligible above pH 5.

effect of polyvalent cations

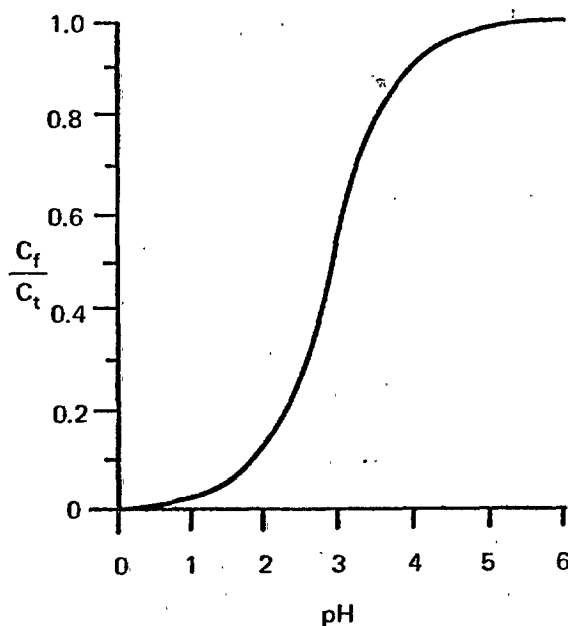
Polyvalent cations such as Si^{+4} , Al^{+3} , and Fe^{+3} will complex fluoride ion. The extent to which complexation takes place depends on the solution pH and the relative levels of the fluoride and the complexing species. In basic solutions, where polyvalent cations complex hydroxide, there will be less fluoride complexation.

glassware

Since fluoride is adsorbed by glass, standardizing solutions should always be stored in plastic containers. For dilute solutions (10^{-4} M or below in fluoride ion), plastic beakers for holding solutions during measurement are recommended.

figure 2

fraction of free fluoride as a function of solution pH, where hydrogen ion is the only complexing species



fluoride measurements

general procedure

1. Insert the reference electrode connector into the reference electrode input on the Specific Ion Meter or pH meter. Make sure the rubber band or plug used to cover the electrolyte filling hole has been removed.
2. Insert the specific ion electrode connector into the electrode input jack.
3. Place both electrodes in appropriate standardizing solutions and record the readings. Wipe the electrodes between solutions to prevent sample carry-over. Stirring of both samples and standards is recommended.

Always blot water from the sensing element with a soft tissue. Never wipe the sensing element except to remove adherent deposits. Scratches on the sensing element will cause slow response to changes in ion level.

4. If a Specific Ion Meter is used, calibrate as recommended in the instrument instruction manual.

If a pH meter is used in the expanded millivolt mode, plot the potential readings on the linear axis of a piece of semilogarithmic graph paper. The values of the standardizing solutions are plotted on the log axis.

NOTE: Certain types of expanded scale pH meters use the pH calibration control on the millivolt ranges as well as in the pH mode. This can cause considerable confusion unless the meter is zero calibrated. This is done by inserting a shorting lead between the glass electrode input jack and the reference electrode jack, and setting the calibration control so that the meter reads zero in the millivolt mode. Now readings taken on the positive and negative millivolt ranges should agree.

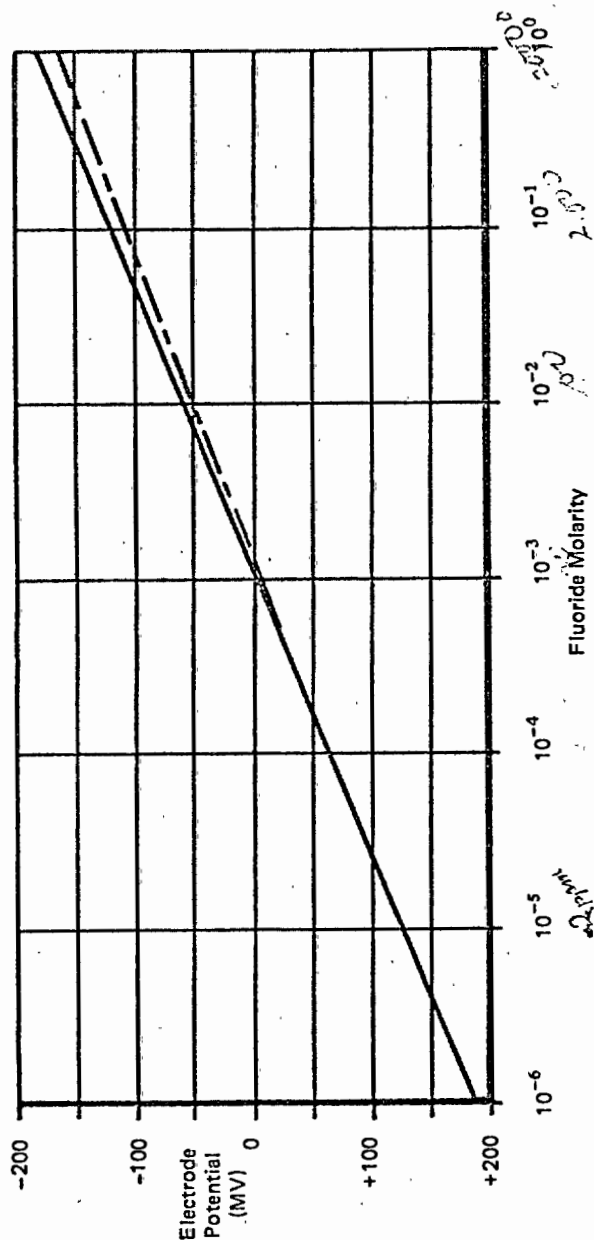
5. Place both electrodes in the unknown solution. Read the value of the unknown on the direct reading specific ion scale on the Specific Ion Meter. With a pH meter, convert the millivolt reading to sample activity or concentration using the calibration curve.

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000059

figure 3

typical calibration curves: electrode potential versus activity (solid line) and concentration (broken line)



Samples and standards should be at the same temperature.

- After use, the electrode may be stored upright in air or in a standardizing solution.

determining fluoride ion activity

The fluoride electrode develops a potential proportional to the logarithm of the activity of the fluoride ion in the sample. At 25°C, the electrode exhibits a 59.16 mv change in potential for each tenfold change in fluoride ion activity. Potentials are increasingly negative in more concentrated solutions; increasingly positive in more dilute solutions. Figure 3 shows the potential response of the electrode to changes in fluoride ion activity.

When the electrode is used with the Model 90-01 Reference Electrode and the 90-00-01 filling solution (which matches the characteristics of the conventional calomel electrode), the meter should read approximately 0 mv in a 10^{-3} M (19 ppm) fluoride ion solution. This reading can vary by as much as ± 20 mv, depending on the particular reference electrode and the solution temperature.

Electrode potentials developed in the same standardizing solution can vary by several millivolts per day. For accurate measurements, the electrodes should be restandardized several times a day, just as is done in precision pH measurements.

Once calibrated in standardizing solutions of known fluoride ion activity, the electrodes respond directly to fluoride ion activity, without regard to sample ionic composition or total ionic strength.

activity standards

For activity measurements, standardizing solutions of known concentrations must be assigned their proper activity values. Table 1 gives fluoride ion activities for sodium fluoride standardizing solutions.

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table 1

single ion fluoride activities in pure NaF solutions
(25°C)

NaF concentration (moles/liter)	fluoride ion activity (moles/liter)
10^{-1}	0.77×10^{-1}
10^{-2}	0.91×10^{-2}
10^{-3}	0.97×10^{-3}
10^{-4}	10^{-4}
10^{-5}	10^{-5}
10^{-6}	10^{-6}

estimating concentration from activity measurements

The activity coefficient of fluoride ion depends on the total ionic strength of the solution. If the approximate sample composition is known, the total ionic strength can be estimated as shown in Appendix I. (Ionic strength can also be estimated from conductivity measurements, as explained in Appendix IV). By using Figure 1 to find the activity coefficient which corresponds to the sample total ionic strength, activity values can be converted to concentration values.

Example: What is the concentration of fluoride in a sample which has a fluoride activity of 0.038 M and is known to have a total ionic strength of approximately 0.2 M?

From Figure 1, the total ionic strength gives an activity coefficient of about 0.70. Therefore:

$$C_f = \frac{A}{\gamma} = \frac{0.038 \text{ M}}{0.70} = 0.054 \text{ M}$$

Therefore, the total concentration of fluoride in the sample can be estimated from the activity, provided all the fluoride present is unbound and uncomplexed. Such estimates can be made only if the sample pH is in the weakly acid to weakly basic range, and if complexing species such as aluminum are absent.

determining fluoride ion concentration (no complexes present)

In samples where complexes are absent, fluoride ion concentration is determined in the same manner as fluoride ion activity, except that the electrode is calibrated in standardizing solutions of known fluoride ion concentration (rather than activity). When making a calibration curve, it will be noted that the concentration curve is not necessarily a straight line and does not necessarily have the same slope as the activity curve. Electrode response as a function of the concentration of pure sodium fluoride is shown as a broken line in Figure 3.

In order to measure fluoride ion concentration in samples that do not have complexes, one of the following methods, depending on the type of sample, is recommended:

1. If unknowns are a) essentially pure solutions of fluoride, and b) have the same relative cationic composition from sample to sample, the electrodes can be calibrated on standards of like composition.

For example, if the fluoride level is to be measured in solutions of essentially pure lithium fluoride, then a calibration curve is drawn (or the Specific Ion Meter calibrated) with pure lithium fluoride standards.

2. If unknowns have a high but essentially constant level of ions other than fluoride, then standards of similar composition can be used to standardize the electrodes in terms of concentration. (That is, standards are used which have the same total ionic strength as the unknowns.)

With samples below 10^{-3} M in total ionic strength, differences in total ionic strength between samples and standards may be as large as a factor of five without resulting in serious errors. In the ionic strength range 10^{-2} M to 10^{-3} M, the total ionic strength of the standards must be within $\pm 50\%$ of the samples for concentration measurements accurate to $\pm 2\%$. For the range 10^{-1} M to 10^{-2} M, samples and standards must be within $\pm 20\%$ for a $\pm 2\%$ accuracy.

3. If unknowns vary considerably in overall composition, an Ionic Strength Adjustor (ISA) is added to both samples and standardizing solutions so that samples and standards are made to have about the same total ionic strength.

It is assumed that the final ionic strength is due essentially to the ISA, and not to the original level of ions found in the unknowns and standards. For samples up to 0.5 M in total ionic strength, an ISA of 2 M KNO_3 is recommended. 9 parts of ISA are mixed with 1 part of sample.

When ISA is used, the activity coefficient of the fluoride ion is held constant, so the electrode exhibits the Nernst slope of 59 mv for a tenfold change of the level of fluoride ion.

fluoride ion concentrations measurements (complexes present)

When complexing agents are present, total fluoride ion concentration can be measured only by destroying the complexes and adjusting the sample solution to a fixed total ionic strength.

1. When the complexing agent is hydrogen (i.e., the pH is below 5), the solution pH is adjusted to the neutral range.
2. When the complexing agent is ferric ion, aluminum ion, etc., the complexing agent is tied up with a polyvalent anion, such as citrate, to release the bound fluoride.

These methods are discussed in detail in the sections on determination of fluoride in drinking water, determination of fluoride in acid solutions, and determination of fluoride in alkaline solutions.

fluoride titrations

The fluoride electrode makes a highly sensitive end point detector for titration of fluoride with lanthanum nitrate.¹ Titrations always measure concentration. They are slower but more precise than direct electrode measurement; precision as high as $\pm 0.2\%$ has been reported.

¹ Lingane, J.J., *Anal. Chem.*, 39 (8), 881-87 (1967)

The method outlined below gives sharp end points in solutions which are above 10^{-3} M in fluoride, and which do not contain more than 1% (based on total fluoride) of species which complex fluoride, such as trivalent chromium, iron, or aluminum, or which complex lanthanum, such as citrate or phosphate.

If the solution to be titrated is in the range 3×10^{-3} M to 3×10^{-4} M in fluoride, distilled water should not be added to the sample in Step 3 below. A larger volume of sample (on the order of 75 ml.) is used. Good end points on solutions as low as 10^{-4} M in fluoride can be obtained if ethanol, rather than distilled water, is added to the sample, because the electrode's limit of detection is about tenfold lower in ethanol solutions.²

The electrode can also be used to detect end points in titrations of aluminum, thorium, etc. with fluoride.

typical procedure

This procedure is suitable for unknowns in the 0.1 M fluoride range. For more dilute unknowns, the lanthanum nitrate and sodium fluoride solutions should be correspondingly dilute.

1. Prepare 0.1 M lanthanum nitrate solution. Dissolve 43 gm. of 'high purity' $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in distilled water.
2. Standardize the lanthanum nitrate solution by titrating against Orion's 94-09-06 NaF standard. Use the millivolt scale on the Specific Ion Meter or the expanded millivolt scale on a pH meter.

Pipet exactly 25 ml. of the NaF standard into a beaker and add about 50 ml. distilled water. Using a buret, add increments of about 0.5 to 1.0 ml. of lanthanum nitrate in the beginning of the titration; about 0.1 to 0.25 ml. in the region of the end point. Continue the titration 3-4 ml. past the end point. Stir throughout the titration.

Locate the end point by plotting, on standard coordinate graph paper, milliliters of lanthanum nitrate solution added versus observed millivolt readings. The point of greatest inflection is taken as the end point.

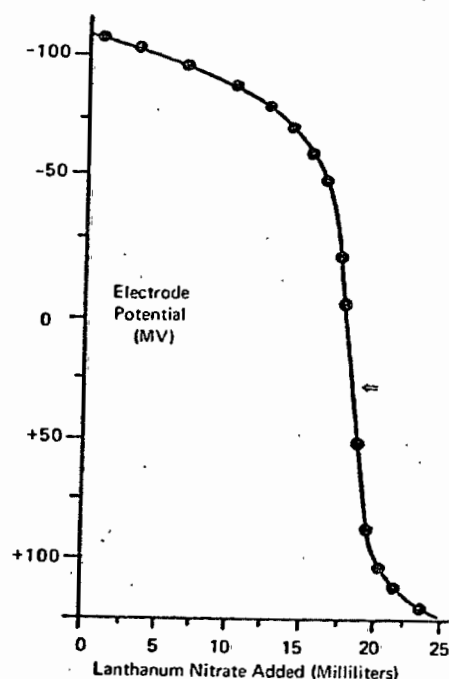
² *Ibid.*

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figure 4

titration of 0.114 M F^- with 0.100 M $La(NO_3)_3$



3. Titrate unknowns. Pipet exactly 25 ml. of the unknown into a beaker and add about 50 ml. distilled water. Adjust the pH to 4.5-7 with HCl or NaOH if necessary. Titrate with the standard lanthanum nitrate solution and determine the end point as above.

4. Calculate the unknown fluoride molarity from the equation:

$$M_F^x = \frac{V_{La}^x V_F^o}{V_{La}^o V_F^x} M_F^o$$

where: M_F^x = molarity of F in unknown

M_F^o = molarity of NaF standard

V_{La}^x = unknown titration end point volume

V_{La}^o = standardization titration end point volume

V_F^x = volume unknown

V_F^o = volume of NaF standard used in standardization titration

determination of fluoride in drinking water

Fluoride in drinking water is expressed as parts per million total fluoride concentration. Since the electrode responds to free fluoride ion, samples must be treated to unbind fluoride if aluminum or iron is present. If the pH is above 9, it must be adjusted to avoid hydroxide ion interference. The total ionic strength of samples and standards must also be held constant for accurate measurements.

All of these problems are eliminated if samples and standards are diluted 1:1 with Orion's Total Ionic Strength Adjustment Buffer (TISAB, 94-09-09). TISAB buffers the solution to pH 5 to pH 6, avoiding hydroxide ion interference, and preferentially complexes any aluminum or iron present. TISAB also provides a high total ionic strength background, swamping out variations in total ionic strength between samples and standards. Calibrated in TISAB-diluted standards, the electrode reports sample fluoride concentration independent of the level or kind of dissolved minerals.

procedure

1. Dilute all standards and samples 1:1 with TISAB. Use original values of standards in calibrating the electrodes.
2. Calibrate the electrodes with 1 ppm and 2 ppm standards, following the instructions in the section on general procedure. Use 0.5 ppm, 1 ppm, and 2 ppm standards if a calibration curve and an expanded scale pH meter are used.
3. Determine the fluoride content of unknowns following the general procedure.

TISAB

TISAB may be purchased as a prepared solution (Orion 94-09-09), or it may be prepared as follows:

Place approximately 500 ml. of distilled water in a 1 liter beaker. Add 57 ml. of glacial acetic acid, 58 gm. of NaCl, and 0.30 gm. of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling), insert a calibrated pH electrode into the solution, and slowly add approximately 5 M NaOH until the pH is between 5.0 and 5.5. Cool to room temperature. Pour into a 1 liter flask, and add distilled water to the mark.

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determination of fluoride in acid solutions

In solutions with a pH below 5, hydrogen ion complexes a portion of the fluoride ion, forming HF or HF_2^- , which cannot be detected by the electrode. To free the complexed fluoride, the pH of the solution must be adjusted into the weakly acidic to weakly basic region before making the determination. A strong base, such as sodium hydroxide, should not be used for pH adjustment, since the total ionic strength of the adjusted samples and standards will vary according to the original solution pH. (Variations in total ionic strength affect the accuracy of concentration measurements.) Dilution with a large excess of sodium acetate, on the other hand, buffers the pH to above 5 and helps to fix the total ionic strength of samples and standards to the same level.

procedure

1. Prepare 15% sodium acetate. Dissolve reagent grade sodium acetate (CH_3COONa) in distilled water. Prepare in sufficiently large quantities to dilute all samples and standards.
2. Prepare a background solution containing all components except fluoride. Use this solution to prepare standards.
3. Prepare standards in the concentration range of the unknowns by adding fluoride to the background solutions. If a Specific Ion Meter is used, two standards are needed. (See Appendix V.) If a calibration curve is to be drawn, three standards should be prepared.

Dilute each standard 10:1 with the sodium acetate solution (9 parts sodium acetate and 1 part standard). Prepare fresh standards every two weeks if standards contain less than 10 ppm fluoride.

4. Calibrate the electrodes, following the instructions in the section on general procedure.
5. Measure unknowns. Dilute each unknown 10:1 with sodium acetate before performing the determination.

NOTE: In many cases standards need not be prepared from background solutions. If a standard prepared from the background solution gives the same reading (after dilution with sodium acetate) as a standard prepared from pure sodium fluoride, then the use of the background solution is unnecessary.

determination of fluoride in alkaline solutions

In basic solutions with a low fluoride content (less than 10^{-4} M at a pH of 9.5 or above), the electrode responds to hydroxide ion as well as to fluoride ion. The potential reading, caused by the concentration of both hydroxide and fluoride ion, is higher than it would be if fluoride alone were present. (Pages 19 and 20 discuss the levels of fluoride and pH values where hydroxide interference occurs.)

Adjusting the pH to between 5 and 6 with a 4 M buffered potassium acetate solution eliminates any hydroxide error and raises the total ionic strength of both samples and standards to the same value. After both samples and standards are diluted 10:1 with the buffer solution, the fluoride ion concentration can be determined in the usual manner.

procedure

1. Prepare 4 M buffered potassium acetate solution. Dilute 2 parts 6 M acetic acid (CH_3COOH) with 1 part distilled water, surrounding the reaction with a water bath. Add 50% KOH solution to the acetic acid slowly, stirring constantly, until a pH of 5 is reached. Prepare in sufficiently large quantities to dilute all samples and standards 10:1.
2. Prepare standards, calibrate the electrodes, and measure unknowns as described in the section on determination of fluoride in acid solutions.

Conc. HAc = 17M

(b) (4)

Appendix Figure 1

Transmission Infra Red Spectrum of High Density Polyethylene

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Appendix Table I

CALCULATED F⁻ INTAKE AMOUNTS

FOR

STANDARD FLUORINATED TOOTHPASTE VERSUS* FLUORINATED CONTAINERS

Toothpaste allowance per tube(F ⁻)	1000 ppm
Size tube used in test	199 gm (Family size)
Wt available F ⁻ /tube	199 mg
Length toothbrush in test	31 mm (bristle length)
Wt toothpaste/brush length	1.85 gm (avg. of 5 measurements)

.....

+Wt fluoride/brushing	1.85 mg F ⁻ (taken into mouth/ brushing)
Wt fluoride/ 3 brushings (recommended daily level)	5.55 mg F ⁻ (taken into mouth/ day)

Fluorinated Containers

100% Market Penetration for totally aqueous diet (1500gm/day)	46.5 mg F ⁻ /day
100% Market Penetration for diverse diet(1500gm/day)	11.2 mg F ⁻ /day
10% Market Penetration for totally aqueous diet (1500gm/day)	4.65mg F ⁻ /day
10% Market Penetration for diverse diet (1500gm/day)	1.12mg F ⁻ /day

* Maximum extracted F⁻ values used for each case of appropriate solvent.

+ These values assume full coverage of brush length with toothpaste.

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ACKNOWLEDGMENT

THE AUTHOR WISHES TO THANK THE FOLLOW-
ING UNION CARBIDE CORPORATION, STERLING
FOREST RESEARCH CENTER PERSONNEL FOR THE
GENEROUS SUPPORT IN GATHERING MUCH OF
THE DATA USED IN PREPARING THIS PETITION.

MS V. A. KANIA

MR. F. D. LUTZ

MS J. S. WALKER

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Yours very truly,

UNION CARBIDE CORPORATION

By: 

Reginald S. Pender
Research Associate

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Submission End

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Indefinite

May 15, 1978

Mr. Reginald S. Pender
Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, NY 10987

Re: Food Additive Petition No. 8B3394

Dear Mr. Pender:

This will acknowledge receipt of your letter dated April 7, 1978, transmitting a petition for Fluorinated Polyethylene as sanctioned material for use in producing, manufacturing, processing, preparing, testing, packaging, transporting or holding foods. This petition has been designated Food Additive Petition No. 8B3394 and has been assigned to Mr. Julius Smith. Further action awaits scientific review.

Jender

Sincerely yours,

MAY 16 1978

Carolyn T. Broadnax
Petitions Control Assistant
Petitions Control Branch
Division of Food and Color
Additives, HFF-334

(b) (5)



000070

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Petitions Control Branch, HFF-334
Attention: Julius Smith

DATE: **MAY 25 1978**

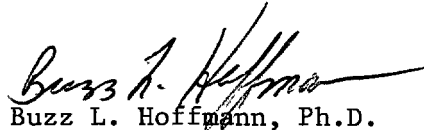
FROM : Chief, Environmental and Economic Impact Staff

SUBJECT: FAP 8B3394-- Environmental Assessment

I have reviewed the "Environmental Impact Analysis" submitted by the petitioner and have determined the proposed action is not exempt pursuant to 25.1(f) and therefore an EIAR will be required in the format specified in 25.1(j).

I have attached for your information a copy of the Environmental Impact Operational Directive of June 1977. Note particularly pages 8-17, which describe the type of information that should be included in an EIAR. You may want to provide a copy to the petitioner to assist in preparing an adequate EIAR.

Please let me know if I can be of further assistance.


Buzz L. Hoffmann, Ph.D.

Attachment

(b) (5)



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MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Petitions Control Branch, HFF-334
Attn: J. Smith

DATE: June 7, 1978

FROM : Residue Analysis & Methods Investigation Branch, HFF-144

SUBJECT: FAP 8B3394 - Union Carbide Corp.

The petitioner requests an amendment to §177.1520 (Olefin polymers) to include the following:

Polyethylene described in paragraph (a)(2) of this section may be surface modified by the action of fluorine gas in combination with other gases as inert diluents, such action leaving the bulk of the polymer unchanged. Fluorine gas shall be used in concentrations not in excess of amounts necessary to achieve the intended technical effect. Maximum extractable fractions and maximum soluble fractions shall not exceed those of polyethylene. Fluoride ion extractives from the polymer surface shall not exceed 5 ppm.

The above is our interpretation of the petitioner's request and we will base our evaluation on this interpretation. However, the petitioner should be required to submit a complete proposed regulation. 171.1(f)

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A. Identity

The subject resin is a surface modified polyethylene which is produced by treatment of polyethylene, in the form of molded containers, with a mixture of fluorine and nitrogen gases. This treatment results in a chemical alteration of the surface of the polymer i.e. it creates a modified, integrally bound surface layer. This surface layer has not been characterized chemically. No information is given on how much fluorine actually becomes bonded to the polyethylene. An IR spectrum of a sample of fluorinated high density polyethylene was provided. The exact reaction conditions (time, temperature, percent of fluorine in the gas mixture) for this sample should be provided.

No details are given on the manufacturing process. Information should be provided on how the containers are treated. Are both surfaces of the container treated or only the inside? The concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation should be clearly spelled out. If other inert gases are to be used besides nitrogen, they should be specified.

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B. & C. Use & Intended Technical Effect

The fluorination process is intended to improve the barrier properties of molded polyethylene containers. Permeation data have been provided to show that the surface modified polyethylene accomplishes its intended technical effect.

The surface modified polyethylene is intended for use with all types of foods. In addition to room temperature applications, their intended uses will include applications where the container will be processed at sterilization temperatures. The approximate maximum thickness of the fluorinated surface layer in containers anticipated for use should be provided.

D. Migration

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Equilibrium extraction studies were performed on 8 oz. polyethylene bottles each of which had 37.99 sq.in. of internal surface area. Two types of containers were tested. One was an irradiated polyethylene bottle for pressurized (aerosol) applications and the other a polyethylene bottle which was not irradiated and is intended for atmospheric pressure applications. (b) (4)

(b) (4)

were filled with the food-simulating solvents (each container holds approx. 230 cc of a given solvent) and subjected to the following conditions to simulate sterilization: distilled water - 250°F/2 hrs; 50% aq. ethanol - 160°F/2 hrs; 3% aq. acetic acid - 212°F/2 hrs; heptane - 150°F/2 hrs. This was followed in each case with continued extraction at 120°F to equilibrium. In all cases, equilibrium was reached within 72 hours.

The amount of fluoride ion (F⁻) in the extracts was determined by potentiometric fluoride ion analysis (F⁻ probe technique). The limit of detection of this method in their experiments was 0.025 ppm of F⁻. The values obtained are given in the following table:

F⁻ Concentration (ppm)

<u>Solvent</u>	<u>Irradiated Container</u>	<u>Non-Irradiated Container</u>
distilled water	(b) (4)	
50% ethanol/water		
3% acetic acid/water		
n-heptane		

(b) (4)

The wall thickness of the containers used in these experiments and the approximate thickness of the modified surface layer in each case should be provided.

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An analysis of the total extractives (with water as the food-simulating solvent under sterilization conditions) was made by an independent laboratory. This analysis showed that all fluoride extracted from the polymer was F^- and no polymerically bound fluoride was detected. The data from this analysis should be provided as well as the exact time and temperature conditions under which this particular extraction was run.

Concerning the values in the table above the petitioner suggests that we evaluate them in light of the allowable limits for fluoride ion in residential and industrial water supplies (1 ppm) and in bottled water (1 ppm).

Conclusions

We do not recommend filing this petition until the following data are provided:

1. A complete proposed regulation. ² BEST ORIGINAL COPY
2. Information on the chemical nature of the modified surface layer and on how much fluorine actually becomes bonded to the polyethylene.
3. The time and temperature of treatment and the percent of fluorine in the gas mixture for the sample on which the IR spectrum was run.
4. Details on the manufacturing process (Are both surfaces treated or only the inside of the container?).
5. The concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation. If other inert gases besides N_2 are to be used they should be specified.
6. The approx. maximum thickness of the fluorinated surface layer in containers anticipated for use; the wall thickness and approx. fluorinated surface layer thickness in the containers used for the equilibrium extraction studies. ⁸⁻³²
7. Data from the analysis of the total extractives by an independent laboratory.

Patricia S. Schwartz

Patricia S. Schwartz, Ph.D.

(b) (5)

000074

July 20, 1978

Mr. Reginald S. Pender
Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, NY 10987

Re: Food Additive Petition No. 8B3394

Dear Mr. Pender:

This refers to your petition referenced above, requesting an amendment to §177.1520 (olefin polymers) for the safe use of fluorine treated polyethylene in producing, manufacturing, processing, preparing, testing, packaging, transporting, or holding foods.

We offer the following comments concerning deficiencies noted in the petition during our preliminary review:

- (a) Information on the chemical nature of the modified surface layer and how much fluorine actually becomes bonded to the polyethylene should be submitted.
- (b) An IR spectrum of a sample of fluorinated high density polyethylene was provided. However, the exact reaction conditions (time, temperature, percent of fluorine in the gas mixture) for this sample should also be submitted.
- (c) No details are given on the manufacturing process. Information should be provided on how the containers are treated. (Are both surfaces of the containers treated or only the inside?)
- (d) The concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation should be clearly spelled out. If other inert gases besides nitrogen are to be used, they should be specified.
- (e) The approximate maximum thickness of the fluorinated surface layer in containers anticipated for use should be provided, including the wall thickness and approximate fluorinated surface layer thickness in the containers used for the equilibrium extraction studies.

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Page 2 - Mr. Reginald S. Pender

- (f) An analysis of the total extractives (with water as the food simulating solvent under sterilization conditions) was made by an independent laboratory. The data from this analysis should be provided as well as the exact time and temperature conditions under which this particular extraction was run.
- (g) We would suggest that a complete proposed regulation be submitted. The proposed regulation should be more specific than the one mentioned on page 16 of the petition.
- (h) Our review of the environmental impact analysis submitted in the petition indicates that the proposed action is not exempt pursuant to §25.1(f) and therefore, an EIR will be required in the format specified in §25.1(j).

To assist you in preparing an adequate EIR, we have attached a copy of the Environmental Impact Operation Directive of June 1977 (Note particularly pages 8-17), and a copy of Environmental Impact Considerations published in the FEDERAL REGISTER of April 15, 1977.

In the meantime, we are evaluating the toxicological aspects of the petition.

Sincerely yours,

Julius Smith
Petitions Control Branch, HFF-334
Division of Food & Color Additives
Bureau of Foods

Enclosures

(b) (5)



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**UNION
CARBIDE**

UNION CARBIDE CORPORATION
TARRYTOWN TECHNICAL CENTER

OLD SAW MILL RIVER ROAD, TARRYTOWN, NEW YORK 10591

CHEMICALS AND PLASTICS
RESEARCH AND DEVELOPMENT

20 October , 1978

Mr. Julius Smith
Department of Health, Education, and Welfare
Food and Drug Administration
Petitions Control Branch
Bureau of Foods
200 C Street, SouthWest
Washington, D.C. 20204

HFF 334

Re: Petition No. 8B3394 (Indirect Food Additive)

BEST ORIGINAL COPY

Dear Mr. Smith;

Enclosed are copies of the correspondence that I had mailed
to the Food and Drug Administration in September.

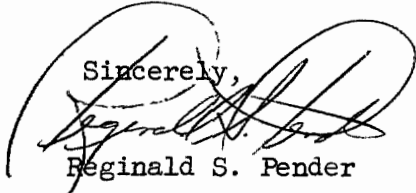
That mailing was responsive to your letter of 20 August citing deficiencies in the petition referenced above. I regret that the original mailing did not reach your desk.

Hopefully the information I am here submitting does in fact reach you and satisfies the comments raised in your letter concerning the submitted petition.

RSP/lb

Encls.;

Sincerely,


Reginald S. Pender

CC: HJL-144
HJL-185

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11-27-78

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PCB
11/16/78

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11/16/78

11/16/78

THE FOLLOWING IS A SUMMARY OF THE INFORMATION RECEIVED FROM THE
POLICE OFFICE OF THE CITY OF NEW YORK ON 11/16/78
RE: [illegible]

ON 11/16/78, [illegible] ADVISED THAT [illegible]
[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

ON 11/16/78, [illegible] ADVISED THAT [illegible]
[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

ON 11/16/78, [illegible] ADVISED THAT [illegible]

11/16/78

ON 11/16/78, [illegible] ADVISED THAT [illegible]
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11/16/78

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UNION CARBIDE CORPORATION
MEDICAL PRODUCTS DIVISION
P.O. BOX 324, TUXEDO, NEW YORK 10987
TELEPHONE: 914-351-2131

September 14, 1978

Mr. Julius Smith
Dept. of Health, Education
and Welfare
Public Health Service
Food and Drug Administration
Petitions Control Branch, HFF-334
Div. of Food and Color Additives
Bureau of Foods
Washington, DC 20204

RE: Food Additive Petition No. 8B3394

Dear Mr. Smith:

This letter is written responsive to your correspondence of July 20, 1978 citing "deficiencies" noted in the above referenced petition. I offer the following comments and references for Union Carbide Corporation.

Generally, the deficiencies cited with the exception of points (f), (g), and (h) of your letter are not in fact deficiencies but are particularly noted in the petition as submitted. I will, however, here respond on a point by point basis.

- (a) "Information on the chemical nature of the modified surface layer and how much fluorine actually becomes bonded to the polyethylene should be submitted."

In response to this noted "deficiency" I refer you to Page 5, Part B, Section 3 where this point is specifically addressed. A copy of this reference is attached and labeled "Exhibit A" with the specific response noted with brackets.

- (b) "An IR spectrum of fluorinated high density polyethylene was provided. However, the exact reaction conditions (time, temperature, percent of fluorine in the gas mixture) for this sample should also be submitted."

The spectrum as referenced here and depicted in Figures 1 and 2 does contain information as to the concentration of fluorine in the gas

(b) (4)

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September 14, 1978

- (c) "No details are given on the manufacturing process. Information should be provided on how the containers are treated. (Are both surfaces of the containers treated or only the inside?)"

The manufacturing process is alluded to briefly in the summary of the petition and generally described in the Environmental Impact section (P16) of the same instrument. I am, however, here submitting a copy of our U.S. Patent #3,998,180 containing a complete description of the process and marked "Exhibit C".

In the normal operation of such manufacturing process both internal and external surfaces of the polymer article are treated. This is not to imply that it is not within our technology capabilities to treat one surface preferentially. The limiting factors would be the need for such single side treatment, the maintenance of final product properties, the economics, and the end-use of a such treated container.

- (d) "The concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation should be clearly spelled out. If other inert gases besides nitrogen are to be used, they should be specified."

To clarify these points, I refer you to Page 3 of the submitted petition, Part A, Paragraphs 4 and 5. Answering the last part of your comment (d), it is stated in Paragraph 4 that "nitrogen gas is the only other ingredient used in this process of surface modification and is used as an inert diluent for the fluorine gas".

As to the comments on gas concentrations, this again is specifically addressed on that same page in Paragraph 5. That paragraph states; "Typical concentrations for this gaseous treatment of polyethylene on a volume basis are (b) (4) for treatment of pressurized use containers and (b) (4) for non-pressurized applications".

(b) (4)

The values are cited repeatedly in the tables such as Tables VII and VIII. Noted copies from the original petition are included with this response and are collectively "Exhibit D".

000079

September 14, 1978

- (e) "The approximate maximum thickness of the fluorinated surface layer in containers anticipated for use should be provided, including the wall thickness and approximate fluorinated surface layer thickness in the containers used for the equilibrium extraction studies."

In responding to this point, I call your attention to the body of the petition Part B (Usage), Section 3 (Maximum Use Level of Additive and Maximum Thickness), Page 5. Here cited in some detail is the information you seek. It is stated that the measurement of the fluorinated surface layer on bottle samples as treated for use "are at best difficult to determine accurately on bottles" because of the surface layer thinness. However, some polyethylene film treated under more exaggerated conditions yields a maximum thickness deposition of about (b) (4) (b) (4). It would be expected, therefore, that as stated, the significantly less severely treated bottles or commercially processed items would yield a substantially thinner surface layer.

The wall thicknesses of bottles used in preparation of the petition were approximately (b) (4) for the aerosol type and approximately (b) (4) for the non-aerosol type bottles.

- (f) "An analysis of the total extractives (with water as the food simulating solvent under sterilization conditions) was made by an independent laboratory. The data from this analysis should be provided as well as the exact time and temperature conditions under which this particular extraction was run.

The extraction from sterilization discussed here is done according to the Food and Drug Administration Guidelines for Requirements of Indirect Food Additives and is so pointed out on Page 10, Paragraph 4 of the petition. On Page 10 also, Paragraph 5, and Footnote 1 on Page 11 is given exact time and temperature conditions for this extraction. It is stated here that the sterilization is for a time duration of two (2) hours and is at a temperature of 250°F.

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- (g) "We would suggest that a complete proposed regulation be submitted. The proposed regulation should be more specific than the one mentioned on Page 16 of the petition."

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Mr. Julius Smith

-4-


September 14, 1978

- (h) "Our review of the environmental impact analysis submitted in the petition indicates that the proposed action is not exempt pursuant to §25.1(f) and therefore, an EIA will be required in the format specified in §25.1(j).

Much of the information to be included in this required EIA is included in the patent (U.S. 3,998,180) which I have previously referred you to and which is included and here again cited. In addition, a rewritten EIA is also included with this correspondence and is so marked.

If any further questions arise or you feel the need to contact me, I am now located at: Union Carbide Corp., Tarrytown Technical Center, Route 100C, Saw Mill River Rd., Tarrytown, New York 10591. My phone number at this new location is (914) 345-2207.

Sincerely,



R. S. Pender

(b) (5)

Enc.

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packaging where such processing is a normal part of the manufacturing operation. Thus, the theorized maximum temperature would be that of high temperature sterilization, i.e. 250°F, during such processing. Time and temperature of normal storage is proposed to be that of duration of current, ordinary, competitive packaging materials for the markets of interest at temperatures ranging to theoretical maximum room temperature of 120°F.

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3. Maximum Use Level of Additive and Maximum Thickness

In the strict sense of interpretation our process does not result in a coating as referenced in this category. Rather, as earlier stated, our fluorination process yields a moderate chemistry alteration on the surface of polyethylene as an integrally bound surface layer. This so-generated layer of fluorinated species affords the major barrier improvement to polyethylene even though this surface is of minimal thickness.

(b) (4)



4. Minimum Contents (Container Volume)

To respond to this point, we would currently propose no minimum container size except that limited by the dictates of practicality of the individual markets of use.

¹ Refer to Fig. 3

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RESPONSE TO POINT (b)

Letter of deficiencies, FOOD ADDITIVE PETITION No. 8B3394

EXCERPTED FROM FOOD ADDITIVE PETITION No. 8B3394

(b) (4)

Transmission Infra Red Spectrum
of Fluorinated High Density Polyethylene
[Reference Spectrum/of Non-Treated HDPE Film in Appendix Figure 1]

(For discussion of this figure see page 5)

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Figure 2

Surface (ATR) Infra Red Spectrum of
Fluorinated High Density Polyethylene Film

(For discussion of this figure see page 5)

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[54] VAPOR DEPOSITION APPARATUS
INCLUDING FLUID TRANSFER MEANS

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118/49; 118/603; 427/237

[51] Int. Cl.² C23C 13/08

[58] Field of Search 118/4, 5, 7, 8, 9, 49,
118/49.1, 602, 603, 50, 50.1; 427/248-252,
237, 166, 167, 107; 55/52, 55; 23/260

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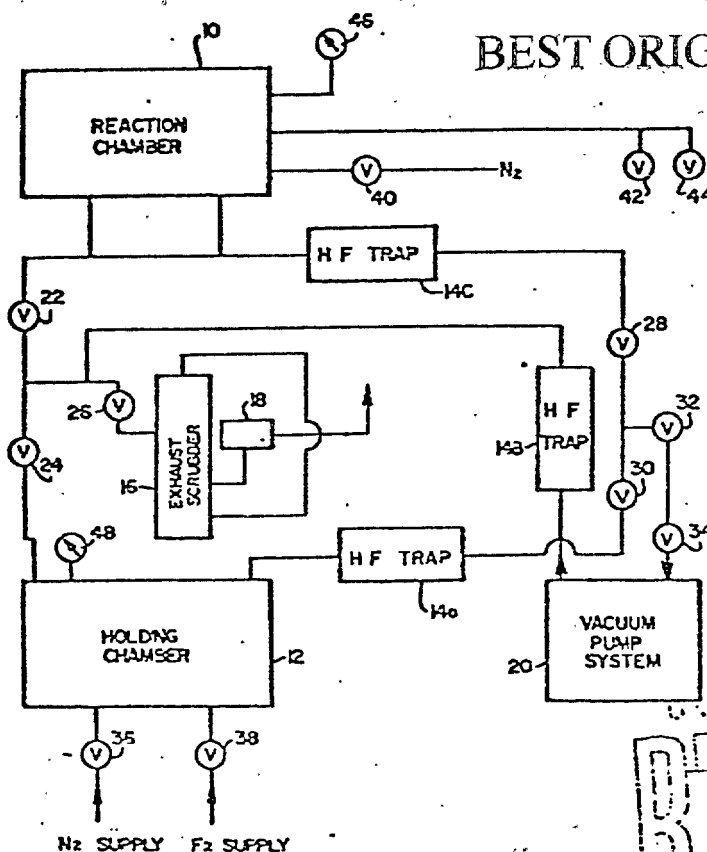
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[57] ABSTRACT

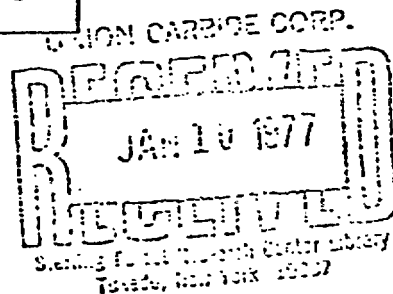
An apparatus and process are provided for the safe, economic and pollution-free exposure of articles to reactive gaseous-fluids to alter their surface characteristics. The articles are exposed to one or more fluids which are transferred back and forth from a reaction chamber to a holding chamber. As the fluids are transferred they pass through a trap designed to remove reaction-by-products without affecting valuable reactant fluids. Since the fluids can be transferred under vacuum and the overall reaction can take place at relatively low temperatures, the process provides a convenient and safe method for handling reactive fluids. The process is particularly useful for the halogenation, for example fluorination, of a variety of articles, such as plastic containers, aerosol bottles and films to improve their barrier resistance to solvents and gases.

5 Claims, 3 Drawing Figures

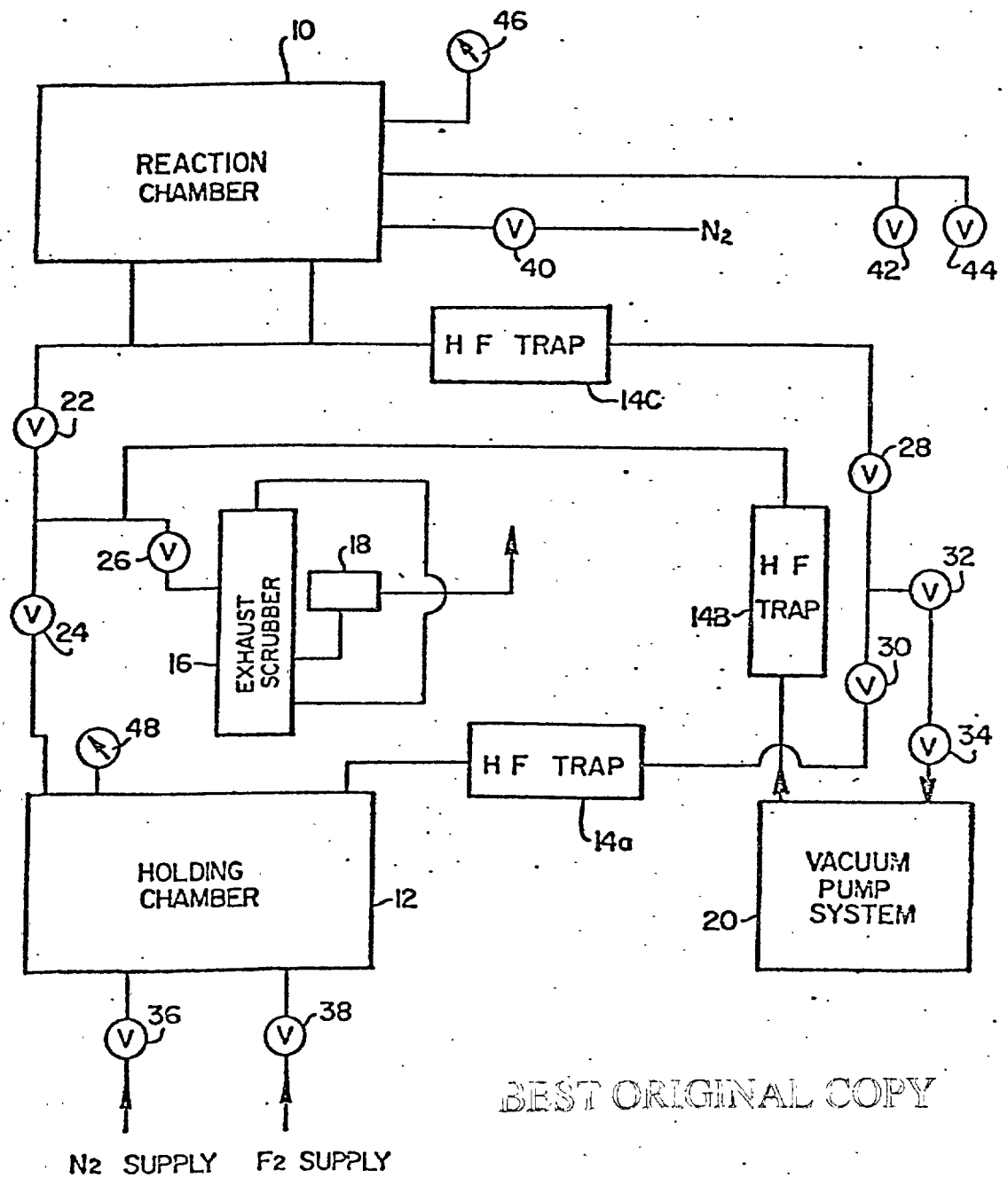


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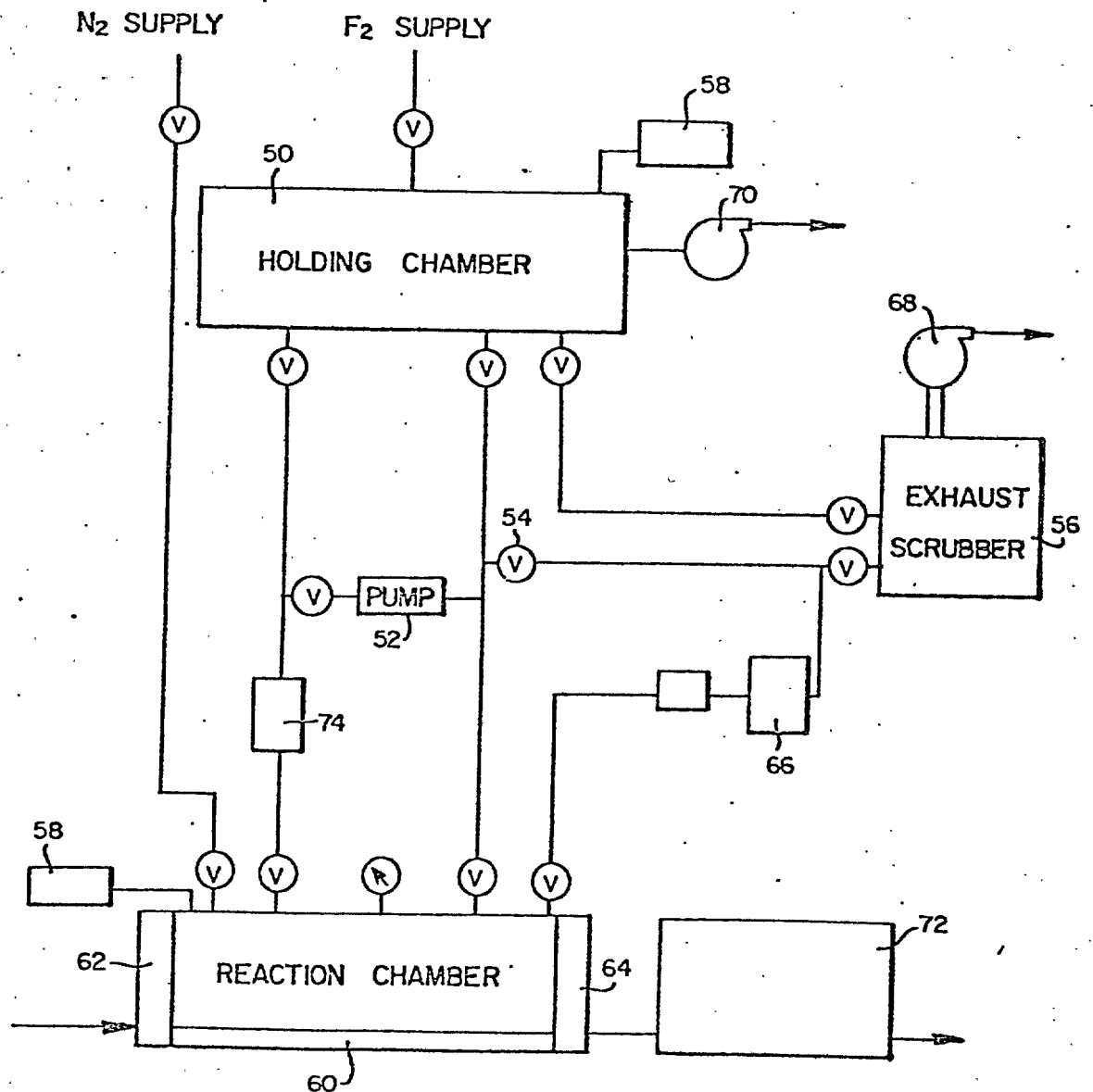
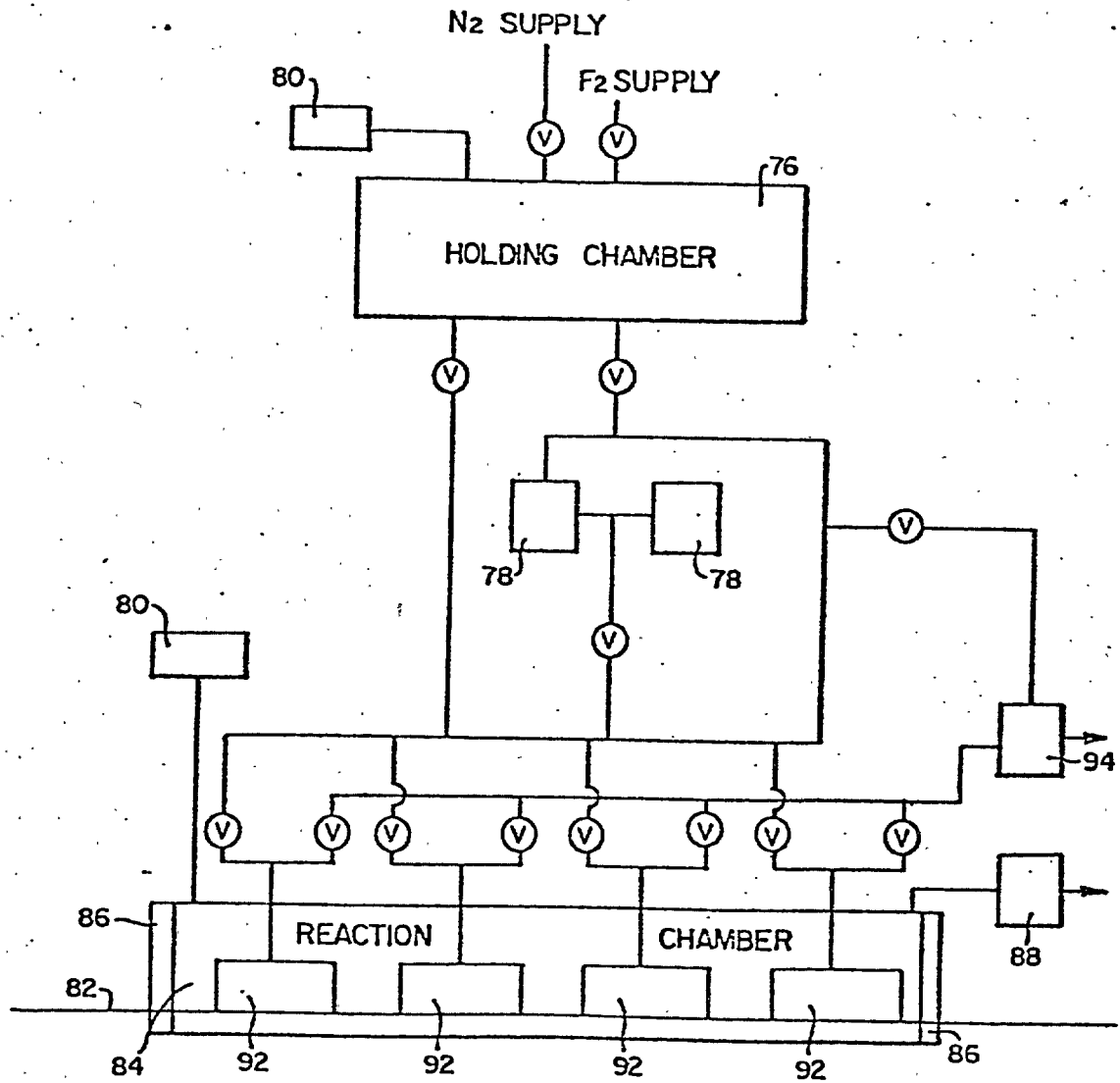


FIG. 2

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FIG. 3



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VAPOR DEPOSITION APPARATUS INCLUDING
FLUID TRANSFER MEANS

In its broad aspect this invention relates to an apparatus for exposing a variety of articles to reactive fluids to alter their surface characteristics. In one aspect, this invention is directed to an apparatus for the halogenation of a variety of articles which is safe, economic and pollution-free. In a further aspect, this invention relates to the fluorination of plastic containers, aerosol bottles and films to improve their barrier resistance to solvents and gases.

A variety of processes and processing equipment are disclosed in the literature relating to the exposure of compositions and articles to reactive fluids whereby their physical and/or chemical properties are altered. For example, the direct halogenation, particularly fluorination, of polymers and polymeric articles is known. By direct fluorination is meant exposure of objects to fluorine gas, either pure or diluted with inert or reactive diluents and additives. In contrast, there is extensive additional art on fluorination of non-polymers, such as organic compositions, metals and the like, or the reaction of materials with fluorinating agents which do not contain elemental fluorine such as hydrogen fluoride, sulfur tetrafluoride, and the like. The literature covers both mechanical and chemical aspects, such as halogenation equipment and its fabrication as well as a wide variety of chemical processes.

Direct fluorination is usually carried out by two methods. In the first, the object, or chamber containing the object, is full of one gas and that gas is gradually displaced by passing in fluorine. In the second general method, the chamber or object is evacuated then fluorine is bled in gradually. Both methods are disclosed in U.S. Pat. No. 2,811,468 which issued Oct. 29, 1957 to S. P. Joffre. In either method, the fluorine which passes through or remains after reaction is flushed out to an absorber or scrubber for disposal. There are no provisions for recycling and reusing valuable unreacted fluorine, nor provisions for removing hydrogen fluoride or reaction-by-products from the fluorine during recycling.

Among the types of apparatus disclosed for fluorination is that illustrated in Pinsky et al. Modern Packaging, 33, P. 130 (1960). This reference shows two tanks which are used independently as a flow-through or as a one-tank vacuum apparatus. Fluorine is not transferred back and forth in the apparatus disclosed.

In another literature article by G. C. Straty and R. Prydz, Rev. Sci. Instrum., 41 (8), 1223-7 (1970), there is described an apparatus for accurate measurements of pressure-temperature-volume behavior of fluorine. Fluorine gas is transferred back and forth between compartments by conventional vacuum line techniques using liquid nitrogen cooling to create suction. Since the intent of the study is to determine pressure-temperature-volume relationships of fluorine, no provision was made for carrying out any reaction in the apparatus. Indeed, every attempt was made to avoid reaction.

Several other references disclose fluorination apparatus. In general, however, these are devices for contacting hydrogen fluoride or fluorine with nuclear fuels to dissolve them, or for reacting uranium with fluorine to make uranium hexafluoride gas. Liquid or fluidized bed flow-through units are common; however, fluorine consumption is large and no recycle systems were disclosed.

Extensive chemical literature also exists on chlorination and, more generally halogenation of polymers. Most is addressed to thorough chlorination of finely divided resin to produce chlorinated polyethylene or chlorinated polyvinyl chloride resin. Gas phase fluidized bed and liquid phase reactions are common. A free radical initiator or UV light is often added.

Since the aim of the chlorination reactions is different, the apparatus and process do not correspond to that used for surface fluorination as hereinafter described.

Several U.S. patents have been granted on technology for treating plastic containers with SO_2 to reduce permeation of organic liquids through the walls. For example, see U.S. Pat. Nos. 2,832,699; 2,937,066; 3,542,746; 3,586,569; 3,592,724; and 3,613,957.

The apparatus of this invention provide numerous advantages over the conventional approaches to direct fluorination as described in the literature for flow-through and single tank vacuum processes. In a flow-through apparatus, such as that of the type disclosed by the aforementioned Joffre patent, the objects to be surface treated are placed in a closed reaction chamber, containing air at atmospheric pressure and the air is displaced to the desired percentage by introducing the surface treatment gas to the interior of the reaction chamber. Since this is done by the gradual replacement of air within the reaction chamber by pressurized surface treatment gas, the object must be exposed to increasing percentages of surface treating gases in coming to the preferred percentage. It is also apparent that a quantity of treating gas will be wasted in flushing out some of the gas in the chamber. In this case, atmospheric air must be acceptable as being present during the treating cycle. If all air is to be excluded, then large quantities of treating gas must be used to purge the air from the chamber. It is apparent that the objects to be treated tend to be exposed to laminar flow of the treating gases.

In a multiple tank system air is removed by means of a vacuum to a predetermined pressure. In one preferred condition this is about 1 Torr absolute pressure, but the pressure is not narrowly critical.

The surface treating gas, contained within a holding chamber separate from the reaction chamber and composed of the desired percentages of treating gases can now be introduced into the reaction chamber through any controlled means so that the reaction chamber can be pressurized in a desired and controlled manner. The pressure conditions are a function of the volume of the treating gas holding tank, and the initial pressure in the reaction chamber. If it is desired (for safety) that the pressure never exceed 1 atmosphere in both the holding chamber and the reaction chamber, then the holding chamber and reaction chamber are made to be of essentially equal volumes. Pressure between the two chambers is then equalized by means of vacuum pumping. Also the holding tank can be lowered to a low absolute pressure for later transfer of the gas back from the reaction chamber to the holding chamber. Contact between the treating gas and object is easily made turbulent, permitting better contact of the entering reactants with all surfaces of the objects to be treated.

A further disadvantage for the flow-through systems described in the literature is that the exact desired time of exposure to a preferred mixture can be achieved only with difficulty. For instance, good mixing during displacement of air with a reactive gas could be pre-

vented if objects are in the chamber. In contrast, in the present process atmospheric air is removed by means of a vacuum pump to a known pressure. Treating gas mixtures, prepared in advance and kept in the holding tank, can now be precisely introduced into the reaction chamber permitting controlled and determined reaction times. Since little gas remains to be displaced, there are no mixing problems.

Another disadvantage of the flow-through system is that all gases pass to a disposal unit. Either they must be discharged with no recovery or absorbed or chemically altered so that the desired gases can be recovered by regeneration or chemical treatment.

As described in this invention treating gases are removed from the reaction chamber to the holding chamber for later use. The surface-treating-gas-mixture can be brought to a desired vacuum in the reaction chamber so that the residual gas in the reaction chamber is at a low level.

An important part of the two chamber system is elimination of by-products. If by-products of the reaction are built up in the treating fluid, they may interfere with some part of the process. A "scrubber" or "trap", selective for by-products, can be installed in the transfer line between the chambers. Thus, the transfer step may include a "purification" step. An alternate concept may have the trap in a side "loop" through which reaction gases are circulated. Although this alternative is more complicated, and requires additional apparatus, it may be desired in some circumstances.

Both the flow-through system and the vacuum system can be purged with air or inert gas to permit safe access to interior of the reaction chamber. The waste gases and purge gases from all systems flow to an absorber or scrubber aimed at rendering them harmless before release to the environment, however, the use of a holding chamber in the two tank vacuum transfer system means that the exhaust gas scrubber need not treat so much gas as in the other approach. Thus, a smaller, more economical unit may be used. This feature also makes it much easier to assure that the waste gases emitted to the environment meet emissions standards.

It is therefore an object of this invention to provide an apparatus for the exposure of a variety of articles to reactive fluids whereby their surface characteristics are altered. Another object of this invention is to provide an apparatus and process which is safe, economic and pollution-free. A further object is to provide an apparatus for the halogenation of a variety of articles. A still further object is to provide an apparatus wherein the reactant fluids are transferred to and from the reaction chamber by vacuum means. Another object of this invention is to provide an apparatus which transfers reactants by means of a vacuum technique in which substantially elevated pressures of dangerous materials are never attained. Another object of this invention is to provide an apparatus wherein reaction-by-products are removed and expensive reactant fluids are conserved. A further object is to provide an apparatus for the fluorination of plastic containers, aerosol bottles, films and the like.

Another object of this invention is to provide an apparatus for introducing reactive gas mixtures from a holding chamber to a reaction chamber in a manner which controls pressure and volume. A further object is to provide an apparatus for injecting reactive gas mixtures directly to the interior of large molded objects so that the reaction is at substantially atmospheric pres-

sure and which minimizes the dilution of the reactive gas mixture with residual air normally contained within the molded object. A still further object is to provide an apparatus for vacuum evacuation of large molded articles prior to exposure to a reactive fluid without collapse of the large article. Another object of this invention is to provide an apparatus for containing a reactive fluid, such as fluorine gas, within the apparatus and thereby minimizing the possibility of the escape of the gas to the atmosphere. A further object is to provide an apparatus whereby pressure build up by inadvertent rapid or violent reaction is safely released by passing the vented gases through scrubbers to render them non-hazardous. These and other objects will become apparent to those skilled in the art in the light of the teachings herein set forth.

In its broad aspect, this invention is directed to an apparatus for exposing articles to reactive fluids to alter their surface characteristics. The apparatus is comprised of:

- a. a sealed holding chamber having conduit means connected to at least one source of fluid, and optionally, access means for the introduction and removal of articles,
- b. a sealed reaction chamber having sealable access means for the introduction and removal of articles,
- c. second conduit means connecting the holding chamber and the reaction chamber, and
- d. transfer means disposed in the second conduit means and capable of creating a pressure differential between the holding chamber and the reaction chamber. The apparatus can also be equipped with pressure control means, means for monitoring the concentration of reactive components, and separation means of reaction-by-products.

The apparatus of this invention is conventionally employed for altering the surface characteristic of articles by exposing them to a fluid at an essentially predetermined composition, wherein the fluid is comprised of, or contains, one or more components which are reactive with the surface of the articles. In essence, the process comprises the steps of:

- a. admitting to an apparatus comprised of at least one holding chamber, and at least one reaction chamber, a fluid comprised of a known concentration of one or more components,
- b. admitting to a reaction chamber which has fluid transfer means to and from said holding chamber, one or more of the articles to be treated,
- c. adjusting the pressures in at least one of the holding and reaction chambers so that the pressure in the holding chamber is greater than the pressure in the reaction chamber,
- d. allowing the pressure to equalize between the holding and reaction chambers by the transfer means and whereby fluid is transferred from the holding chamber to the reaction chamber,
- e. optionally, adjusting the pressure in at least one of the holding and reaction chambers so that the pressure in the reaction chamber is greater than the pressure in the holding chamber,
- f. allowing the components to react with the articles,
- g. optionally, allowing the pressure to equalize between the holding and reaction chamber by the transfer means and whereby the fluid is transferred to the holding chamber from the reaction chamber,
- h. adjusting the pressure in at least one of the holding and reaction chambers so that the reaction chamber is

less than the pressure in the holding chamber, and thereafter,

i. removing said articles from said reaction chamber.

A better understanding of the invention will be had by referring to the following description and changes wherein:

FIG. 1 is a schematic diagram of the apparatus of this invention.

FIG. 2 is a schematic diagram of a production scale treating unit.

FIG. 3 is a schematic diagram of a production scale unit useful for treatment of the interior of large objects.

With reference to the drawings FIG. 1 is a schematic diagram of a simplified version of the apparatus of the invention.

Reaction chamber 10 is a cylindrical stainless steel vessel of approximately 16 inches inside diameter and 24 inches inside length. One end is closed by a circular door with a rubber sealing gasket. The chamber has a water jacket permitting heating or cooling of the chamber walls.

Holding chamber 12 is a stainless steel cylinder of approximately the same size as reaction chamber 10. In the examples it was chosen to be about 10 percent larger than the reaction chamber. Thus, when gas was initially transferred and pumped into the reaction chamber, the holding chamber did not have to be evacuated to near 1 Torr. Instead, it had only to be evacuated to approximately 70 Torr while the reaction chamber was pumped to 1 atmosphere. This procedure has the advantage that the vacuum pump is not pumping in its slowest, least efficient, low pressure range; as a result, the reaction chamber can be brought to 1 atmosphere of reactive gas more quickly.

When the reactive gas is fluorine one or more traps are employed to absorb hydrogen fluoride and by-products of the reaction. Hydrogen fluoride trap 14 can be located at one or more positions as indicated by 14a, 14b and 14c and is a stainless steel cylinder approximately 5 inches in diameter and 15 inches long. It was filled with pellets of sodium bifluoride, activated by heating with a nitrogen purge. It is thus apparent that several alternative locations for trap 14 are possible. For example, the trap can be located between chamber 10 and valve 28 as indicated by 14c. It is only important that the trap be situated so that the reactive fluid containing by-products can flow through the trap.

Effluent scrubber 16 is a vertical stainless steel cylinder approximately 6½ inches in diameter and 48 inches high. It contains circulating aqueous 20 percent potassium hydroxide solution through which the exhaust gases are passed. Drop catcher 18 removes droplets

contained in the exhaust gases prior to venting to the atmosphere. Vacuum pump 20 aids in transferring the gases to and from reaction chamber 10 and can be comprised of, for instance, a combination of a piston-type pump and a Rootes-type blower as hereinafter described. Valves 22, 24, 26, 28, 30, 32 and 34 control the flow of the gases to and from holding chamber, reaction chamber, traps and scrubber. Valves 36, 38 and 40 control the entry of reactive and inert gases. Valves 42 and 44 permit monitoring of the gases in the reaction chamber. Additional monitoring valves, not shown, are also present to monitor the holding chamber. Gauges 46 and 48 monitor pressures within the reaction and holding chamber.

When fluorine or certain other components are the reactive fluid to be used in the process of this invention, it is necessary to "passivate" the apparatus. Passivation can be accomplished by the usual method known to those skilled in handling fluorine. That is, a small amount of fluorine at a low flow rate can be introduced into the apparatus and all surfaces exposed to gradually increasing concentration of fluorine until it ceases to react with the surfaces and passes through the apparatus unchanged.

In order to demonstrate the operation of the unit for one particular sequence of steps which can be employed, Chart A below show the positioning of the valves. The sequence of operations described in Chart A is that normally used to operate the simplified apparatus shown in FIG. 1. Consideration of that drawing will reveal that alternate ways of carrying out the process are embodied in the apparatus. For instance, pressure equalization (Steps 6 and 9) could be carried out through valves 22 and 24 if desired, or through the vacuum pump. Thus, the process of using the apparatus is not to be limited by the specific series of steps shown in Chart A, but rather, is illustrative of the process of the invention. Also, during normal operation, Steps 3 through 14 may be repeated several times. If desired, samples of the reaction mixture may be taken at a sampling manifold attached to the reaction and/or holding chamber. It is also evident from a consideration of Chart A and FIG. 1 that in this particular simplified apparatus, in which the HF trap is located at 14a, HF and by-products are scrubbed from the gas mixture as the mixture passes from the holding chamber to the reaction chamber rather than the reverse. It is apparent that either procedure is feasible and the invention is not limited to either one.

In Chart A below the vacuum pump is on at all times during which the unit is operating. "C" indicates that the particular valve is closed and "O" that the valve is open.

CHART A

VALVE LOGIC DIAGRAM FOR SURFACE TREATMENT APPARATUS

Operation	Valve:	Position of Valves and Door						Reaction Chamber Door
		22	24	26	28	30	32	34
1. Evacuate Holding Chamber		C	C	O	C	O	O	O
2. Fill Holding Chamber from F ₂ and N ₂ supplies		C	C	C	C	C	C	C
3. Load Reaction Chamber		C	C	C	C	C	C	O
4. Evacuate Reaction Chamber		C	C	O	O	C	O	C
5. Prepare to equalize pressure through HF trap		C	C	C	C	C	C	C
6. Equalize Pressure		C	C	C	O	O	C	C
7. Pump F ₂ mixture into Reaction Chamber		O	C	C	C	O	O	C
8. Carry out Reaction		O or C	C	C	C	C	C	C
9. Equalize Pressure		O or C	C	C	O	O	C	C
10. Pump gases from Reaction Chamber to Holding Chamber		C	O	C	O	C	O	C
11. Fill Reaction Chamber with N ₂ (Optional Settings)		C	C	O	O	C	O	C

CHART A-continued

VALVE LOGIC DIAGRAM FOR SURFACE TREATMENT APPARATUS

Operation	Valve:	Position of Valves and Door							Reaction Chamber Door
		22	24	26	28	30	32	34	
12. Pump Reaction Chamber Contents through Scrubber		C	C	O	O	C	O	O	C
13. Fill Reaction Chamber with N ₂		C	C	C	C	C	C	C	C
14. Remove Treated Objects		C	C	C	C	C	C	C	O

In practice, the process can be effected over a wide range of conditions. Although, for the most part, the operating conditions are not critical, care should be taken since the process involves the use of reactive and toxic gases.

The amount of reactive fluid, such as fluorine, employed can vary over a relatively wide range and is largely a factor of the article being treated. Hence, most any concentration of fluorine gas or other reactive fluid in another gas may be used provided the mixture can be safely prepared. Normally, a range of from 1 to 100 percent by volume has been found to be useful. However, the most preferred portion of this range for some processes is 5 to 80 percent. Under some circumstances, where "light" exposure is desired, concentrations as low as 0.001 percent fluorine (or other gas) or even lower may be desirable. The fluorine may be diluted with essentially inert gases such as nitrogen or helium. At higher concentrations of fluorine or other reactive fluids, reactions tend to be more violent and the apparatus may erode or react, so that where possible, lower concentrations are preferred.

A reactive gas such as fluorine may be mixed with one or more inert or reactive diluents. For example, fluorine can be mixed with oxygen, sulfur dioxide, chlorine, bromine, nitrous oxide, a mixture of chlorine and oxygen, certain organic monomers and the like. Although, the materials of construction may vary depending upon the gases employed, the overall process is the same.

Although 1 Torr is preferably the level to which the chamber is evacuated, the pressure is not narrowly critical. It is chosen by considering safety and economic factors such as the amount of residual gases released when the door is opened, or the amount of residual gas left to mix with the treating gas. For especially careful work, the chamber might be evacuated with elaborate pumping means to 0.001 Torr or less. A useful upper limit is about 700 Torr. The pressure most often useful is from about 0.1 to about 10 Torr.

For safety reasons it is often desirable to keep a chamber containing reactive gases at less than 1 atmosphere pressure so that any leaks are inward. Thus, use of vacuum as a gas transfer means is a particularly attractive safety feature. However, to accelerate the reaction, pressure may be raised to as high as 600 psig (of fluorine) or higher, with some risk of excessively violent reactions. The preferred range is from about 0.1 to about 2 atmospheres.

Preferred temperature conditions for conducting the process (when the reactive fluid is fluorine gas) are within the range of from about 0° to about 100° C. Higher temperatures might be used for articles such as those composed of graphite, wherein temperatures as high as 700° or 800° C. could be used. A particularly preferred temperature range for plastic articles is from about room temperature to about 80° C. This range will

be generally useful for other fluids but may vary in some cases, depending on the reactivity of the fluid.

The temperature range is not narrowly critical and will be limited by the tendency toward excessive reaction at high temperature, and of slow reaction or condensation or freezing of the reactive fluid at low temperature.

The desired treatment time at the aforementioned temperatures is not narrowly critical. For treatments with fluorine as shown in examples, times from 0.5 to 50 minutes are preferred. If extensive fluorination reaction is desired, hours or days may be used. Conversely for "light" treatments, a few seconds of exposure or even fractions of a second may be sufficient. These treatment times can include the time required to adjust the reaction chamber to a constant pressure. However, in the examples the times indicated refer only to the time at which the reaction chamber is at the constant pressure.

As hereinbefore indicated the apparatus of this invention can be utilized for the treatment of a wide variety of articles. For example, articles comprised in whole or in part of inorganic, or organic materials or combinations thereof can be treated by the process and in the apparatus of this invention. The apparatus can, for example, be used to "passivate" metal tubing before installing the tubing in other fluorination apparatus.

In a preferred embodiment the invention is directed to an apparatus for treating plastic articles with elemental fluorine, and inert or reactive diluents, for the purpose of altering their surface characteristics. The invention is particularly applicable to articles comprised of, in whole or in part, polymeric organic compositions. For example, containers of high and low density polyethylene, polypropylene, polybutylene, polystyrene, and a great variety of other organic polymers can be treated. Illustrative polymers include poly(vinyl chloride), cellulose acetate and even partially fluorinated materials such as poly(vinyl fluoride). In addition to plastic bottles and containers, films (rolled or flat), plaques, tanks, drums, aerosol containers, extruded solid shapes, gloves, tires, fibers and other plastic articles can be treated. Also, textiles, fabrics, clothing, paper, cardboard and the like can also be treated to alter their properties, in particular, surface characteristics.

With suitable adjustment of treatment conditions (from mild to severe) to suit the article being treated and properties desired, almost any solid composition such as plastic, metal, paper, fabric, and the like and some liquid compositions may be treated by the apparatus of this invention. Limitations on substances or articles would include difficult handling due to fluidity, vapor pressure (evaporation during evacuation would be undesirable) and the like. However, it is the major purpose to treat organic solids and polymeric solids.

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It is also apparent from consideration of the invention that very large or very small objects of a variety of sizes and shapes might be treated. To further visualize the treatment of such objects, FIGS. 2 and 3 depict other embodiments of this invention.

FIG. 2 is a schematic diagram for a production scale treating unit. To start the operation the air in gas mixture holding chamber 50 is evacuated by vacuum pump 52 through valve 54 and to atmosphere through the scrubber column 56. Fluorine and nitrogen are then expanded into holding chamber 50 from known volume cylinders. The gas mixture is analyzed by instrument 58, and the chamber 50 is now at atmospheric pressure.

The objects to be fluorinated are in position of the transfer device ready to move into the reaction chamber 60, and the unit is now in the ready position. To load chamber 60 door 62 opens to admit new product and door 64 opens to permit the treated objects to leave. These doors are interlocked so that pump 66, blower 68 and fan 70 must be running before the doors can be opened. The transfer device now loads new objects into reaction chamber 60 and unloads treated objects to wash chamber 72. The transfer device may include hand loading.

Air is now evacuated from chamber 60 through the proper sequence of valves and by vacuum pump 66. This air evacuation sequence continues until the pressure in chamber 60 is lowered to approximately 1 Torr. At the end of this period the proper valves open and the gas mixture contained in chamber 50 enters chamber 60 so that both chamber 50 and chamber 60 are at $\frac{1}{2}$ atmospheric pressure.

During the next sequence and through the proper valves the atmosphere in chamber 50 is transferred to chamber 60 so that 60 is at atmospheric pressure and chamber 50 is under vacuum. Pump 52 is used for this transfer. At the end of this period the fluorine gas mixture is allowed to dwell within chamber 60, for instance, for 60 seconds.

At the end of this dwell period, the procedure is reversed and the fluorine atmosphere is allowed to flow back to evacuated chamber 50 through an HF trap 74 so that again both are at approximately $\frac{1}{2}$ atmospheric pressure. Next the atmosphere remaining in chamber 60 is pumped back to chamber 50 through an HF trap 74, so that this chamber returns to atmospheric pressure and the pressure in chamber 60 goes to approximately 1 Torr.

A final period is allowed to continue evacuation of chamber 60 to the scrubbing system through the vacuum pumps. Dry air can be purged into the chamber to effect further dilution of residual gas if this proves necessary.

As mentioned previously, this description is a description of the general process. Modifications as described later will suit particular objects to be fluorinated. For example, large volume items, such as tanks or 55 gallons drums could be treated by directly loading the fluorine atmosphere to the inside of the container. Film could be treated in an essentially atmospheric condition within the reaction chamber 60. Small containers could be treated essentially as described. In a production operation all valves can be automatically sequenced so that once the process begins all steps will follow in programmed steps.

With further reference to FIG. 2, reaction chamber 60 is designed to operate from approximately 1 Torr absolute pressure to 200 psig. At each end of the cham-

ber are automatic doors which at the proper time open to permit objects to enter and leave. The doors are arranged to permit the chamber to go to 1 Torr, and the preferred maximum operating pressure is one atmosphere, but approximately 2-3 atmospheres (14.7-29.4 psig) may be used. One reason for operating at pressures down to 1 Torr is that only a small amount of fluorine or hydrogen fluoride need be removed in a purge step.

As with all hardware items in the apparatus, the suitable materials of construction are not narrowly critical. As is well known to those skilled in the art, exposure of many metals to gradually increasing levels of F_2 concentration "passivates" the metal surfaces making them resistant to further reaction with fluorine. Thus, metal items may be iron, steel, aluminum, copper, brass, or stainless steel. Where high-temperatures are expected (over 100-200°C), monel metal, nickel or high nickel content alloys are preferred.

Flexible gaskets can be made of rubbers or of fluorinated elastomers such as VITONTM or FLUORELTM. Plastic parts are frequently made of TEFLON or KEL-F plastics. Only where factors other than fluorine contact must be considered must other limitations be made on materials. For instance, a liquid scrubber for HF and F_2 , mentioned below, would not be made of a material that reacts with alkali such as aluminum.

Wash Chamber 72 is an adjunct to the main part of the invention and may not be always needed. In FIG. 2, it is immediately behind and adjacent to chamber 60. In it, the product is water-washed for a period of several minutes to remove traces of fluorine or HF. This chamber also can be traversed by an indexing conveyor which at the end of the cycle time can move the product out of the wash chamber to be placed in inventory. Materials of construction are not narrowly critical and can be plastic or stainless steel.

Gas Holding Chamber 50 is essential to the invention. This is a tank designed to approximately equal the capacity of reaction chamber 60. It serves as the holding tank for the gas atmosphere. The atmosphere is equalized when desired between chamber 60 and gas holding chamber 50 through appropriate valving and connecting means.

Materials of construction and design pressures are the same as for the reaction chamber; no doors are needed. Alternatively, the holding chamber could resemble the reaction chamber, providing two reaction chambers.

Vacuum pumps 66 and 52 are designed to evacuate chamber 60 from atmospheric pressure to approximately 1 Torr absolute. Various pumping times (1 second to 30 minutes) may be suitable in particular cases. Any suitable means of creating vacuum may be used, including dry or oil sealed vacuum pumps and cryogenic or absorption pumps. If oil-sealed pumps are used, a halogenated or fluorinated pump fluid is preferred. Oil sealed pumps are often not suitable because of reaction between the oil and the reactive fluid. A dry piston pump (e.g., Corken Pump) and a Roots-type pump are also suitable. A single pump could also replace pumps 66 and 52.

Any suitable means of trapping HF but not F_2 may be used. Such a trap is an important part of the invention unless the amounts formed are so small as not to interfere with the process or apparatus. One example common in the art is a sodium bifluoride pellet packed-bed, filled with $NaF \cdot HF$ which can be activated by heating

while being purged with N_2 . Refrigerated traps may be used. As known in the art, HF absorbed by such traps can be recovered by heating the trap. Material of construction are not narrowly critical, but nickel and its alloys are preferred.

The scrubbing system 56 described in this disclosure, for use with the subject apparatus, is a convenient and economical means of disposing of the small amount of objectionable gaseous fumes before emission from the vacuum transfer system. Such a means is necessary for safe non-polluting operation of the invention; however, the actual treatment of objects could be carried out without such a scrubber if the wastes were not toxic or undesirable.

While a scrubbing method is described below, it is obvious that other methods such as absorption, direct chemical reaction, or other means well known to the art could be employed to absorb noxious wastes.

FIG. 2 shows scrubbing system 56. The system is comprised of a stainless scrubbing tower for scrubbing the gas with an aqueous solution of sodium hydroxide. This solution is fed through the column through a distributor plate and flows concurrently with the gas atmosphere. The reacted stream (now containing sodium fluoride, air and sodium hydroxide) enters the holding tank containing the reservoir of sodium hydroxide. This holding tank is so designed that the air streams must enter the reservoir of sodium hydroxide. The air passes through this solution and out to atmosphere through the second column which is packed with suitable packing. Here the air travels countercurrent to a flow of sodium hydroxide and the remaining traces of fluorine are reacted to sodium fluoride. Other bases (e.g., KOH) will work.

Since the sodium fluoride is partially soluble in water, a stream of the reservoir can be taken to a lime treater where the sodium fluoride is converted to calcium fluoride and the sodium hydroxide regenerated. The calcium fluoride which is insoluble can then be passed to waste as a harmless salt.

FIG. 3 is a schematic diagram of one embodiment of the apparatus and process of this invention which is useful for treating the inner surfaces of relatively large objects, such as 55 gallon drums, gasoline tanks, and the like. A major difference between this embodiment and those previously described is that fluorine is added directly to the interior of the object. A major difference over the previous embodiment of FIG. 2 is the addition of a vacuum pump to equalize the pressure in the reaction chamber to avoid collapse of the object being treated.

With reference to FIG. 3 the process is conducted as follows: gas mixture holding chamber 76 is evacuated through vacuum pump 78. The fluorine and nitrogen are then expanded into chamber 76 from known volume cylinders. The gas mixture can be analyzed by instrument 80, and chamber 76 is approximately at atmospheric pressure. The large objects 92, for instance, polyethylene gasoline tanks, are in position on the indexing conveyor 82 and the unit is now in the ready position. Reaction chamber 84 is equipped with doors 86. These doors are interlocked so that pump 88 must be running before the doors can open. The conveyor is then operated so that the large object move into proper position and the sequence begins. Air is now evacuated from the large objects through the proper sequence valves and by vacuum pump 94. At the same time vacuum pump 88 evacuates the air from

the chamber in order to prevent collapse of the object due to pressure difference. This air evacuation sequence continues until the pressure in the large objects is lowered to about 1 Torr absolute. At the end of this period the proper valves open and the gas mixture contained in holding chamber 76 directly enters the large objects and air or another gas enters chamber 84 so that the pressure in both these objects and in chamber 76 equalizes at $\frac{1}{2}$ atmospheric pressure. During the next sequence and through the proper valves, all of the atmosphere in chamber 76 is transferred to the large objects so that these objects are now at atmospheric pressure and chamber 76 is under vacuum. At the end of this stage the fluorine gas mixture is allowed to dwell within the large objects for e.g., 60 seconds. During all stages of the process, the pressure in reaction chamber 84 can be controlled to a suitable differential between itself and the large objects to minimize leakage, collapse or expansion.

At the end of this dwell period the procedure is reversed, the proper valves open and the fluorine atmosphere is allowed to flow back to evacuated chamber 76 so that again both are at $\frac{1}{2}$ atmospheric pressure. Next the atmosphere remaining in the large objects is pumped back to chamber 76, so that this chamber returns to atmospheric pressure and the large objects are at 1 Torr absolute. Suitable pressure is maintained in chamber 84 by pump 88.

After this stage, the objects are evacuated and gases pass to the scrubbing system through vacuum pump 94. Again suitable pressure is maintained in chamber 84. The unit is now ready for the second loading operation the doors open, the treated large objects move into the wash chamber and the second cycle begins.

As previously indicated an important aspect of this invention is to move fluorine safely and economically from one chamber, initially at or near 1 atmosphere pressure to another, at or near 1 torr. After treatment, the transfer must be reversed. Obviously, a pressure equalization suffices for one half of the pressure change. To pump the remaining fluorine, an oil sealed vacuum pump of any of several mechanical types such as sliding vane, rotary piston, and the like could be considered. Any such pump would be suitable if the gas to be transferred were not so reactive as fluorine, for instance, air or nitrogen. However, even the very inert "Halocarbon" oils are often not suitable for fluorine contact in such applications, as they decompose or explode.

By combining a dry (non-oily) piston-type compressor having low friction piston rings such as graphite rings or TEFLON rings, with a dry (non-oily) vacuum pump, specifically a Rootes-type blower the pressure can be reduced to 1 Torr. By specially modifying the valves, the piston compressor has been made to act as a high quality vacuum pump capable of pumping down to 25-50 Torr; the Rootes Blower in series with it covers the remaining range and pumps down to approximately 1 Torr. A Rootes blower by itself cannot pump over the required pressure range. Thus, depending on the exact pumping characteristics of the piston pump, chamber size, pumping times, and other factors, either one Rootes pump or two in series may be used together with the piston pump. Use of all Rootes pumps would normally not be practical or economical. At least four would be needed in series and the high pressure ones must be very large and expensive.

As previously indicated, and as set forth in the examples, several desirable properties can be imparted to articles treated in the apparatus and by the process of this invention. For the most part, treatment of the articles provides modifications in their surface properties. For example, these include reduced permeability to some types of organic liquids such as xylene, gasoline, and the like. Permeability to oxygen is also reduced. Ability to accept printing inks can be enhanced. Chemical composition of the surface can be altered. Other properties might be conferred or removed, depending on the objects or treatment fluids to be used.

In the following examples, testing for gas permeation rates was carried out by a method described by Brubaker and Kammermeyer in *Anal. Chem.*, 25, 424-426, 1953, with the modifications set forth below. The principle used was identical to the one cited in the article, that is, measuring the permeated gas rate at conditions of constant temperature and pressure, by displacing a liquid in a capillary column. The exit end of the capillary column opens into laboratory ambient conditions. The entrance end of the liquid filled capillary is connected to the low pressure (permeate) side of a supported membrane or film. On the other side of the membrane, a high pressure of gas, typically 100 psig, ranging from 40 to 200 psig, is applied from a suitable source such as a pressurized gas cylinder and gas pressure regulator. Under these circumstances, gas permeates through the membrane or film and displaces liquid in the capillary tube. A calibrated pipette — volume chosen to match the flow rate — is used as the capillary, and the time rate of liquid volume displacement in the capillary is taken as the gas permeation rate. The formula in Brubaker and Kammermeyer is used to convert permeation rate to permeability constant. Because generally large changes in permeation rate are caused by the process of this invention, the very small percentage corrections for different barometric pressures and different room temperatures on different days were neglected.

The modifications of the reference process included the use of colored water in place of mercury as the liquid in the capillary tube. Additionally, in place of a vibrator, the capillary tube was tapped manually. A circular test area of 25.6 square centimeters was used and the film supported on sintered stainless steel. No screen or porous disk was put on the high pressure side of the film. Also the seal between the high pressure side of the permeation testing cell and the membrane was made by an O-Ring instead of a gasket. A short length of thick walled rubber tube connected the outlet of the low pressure side of the cell to the capillary tube.

Liquid permeation rates were typically measured by following the weight loss of a tightly capped container over a period of time.

The following examples are illustrative:

EXAMPLE 1

Into the reaction chamber of the apparatus shown in FIG. 1 were placed high density polyethylene bottles of one gallon capacity and also films of different polyethylenes, 1.2 to 4 mils thick and about 6 by 12 in size. In this example water at room temperature (approximately 23° C) was circulated in the heating jacket. After the door to the reaction chamber was closed, the chamber was evacuated to 1 Torr. During 5 seconds

the chamber was filled to ½ atmosphere pressure with a mixture of fluorine and nitrogen (25% F₂ by volume) by equalizing pressure with a holding tank of approximately the same size, previously filled with approximately 1 atmosphere pressure of the gas mixture. Then the gas mixture from the holding tank was pumped into the treatment chamber during about 40 seconds, raising the pressure to approximately 1 atmosphere. These transfers occurred through the HF trap. The gas mixture was maintained in the treatment chamber for 1 minute, then gas was transferred from the reaction chamber to the holding tank, first by equalizing pressure then by pumping to evacuate the reaction chamber into the holding tank. After the treatment chamber was evacuated to 1 Torr, (during 2 ½ minutes), it was then filled with air again and evacuated again. The samples were removed and the permeation constants were measured as hereinbefore described. The results obtained on the films are set forth in Table I below:

TABLE I

PERMEATION CONSTANT TO METHANE, °CH ₄ × 10 ¹⁰		
	Before Treatment	After Treatment
4 mil commercial LDPE ⁽¹⁾ bag film	283	80
1.2 mil LDPE (0.918 dens, 0.1 M.I.)	534	24
1.5 mil HDPE ⁽²⁾ (0.96 dens, 0.8 M.I.)	86	20

⁽¹⁾ Permeability constant in cc.-cm./sec.-cm.-cm.Hg(AP)

⁽²⁾ Low Density polyethylene

⁽³⁾ High Density polyethylene

The high density polyethylene bottles were also tested to determine changes in permeability to gasoline, by filling them with approximately 2,800 grams of commercial grade gasoline, capping them tightly and weighing them periodically while they stood at room temperature. The results are set forth in Table II below:

TABLE II

GASOLINE PERMEATION LOSSES	
Bottle Treatment	Gasoline Lost After 26 Days at Room Temperature
None	105 g
None	106 g
25% F ₂ in N ₂ at room temperature, 1 minute	21 g

EXAMPLES 2 - 6

An additional series of treatments were carried out in the same apparatus and in a similar manner as that set forth in Example 1. Hot water circulating in the reactor was maintained at a temperature of 66° C. After completion of the fluorination treatment the bottles, which were blow molded of high density polyethylene, were filled with approximately 50 grams of a 1/1 mixture of CF₂Cl₂ and CFCI₃ and capped with a crimped aerosol bottle valve. The bottles were molded to have a wall thickness at the thinnest part of at least 0.065 at the maximum diameter of 2 ¼" in order to easily contain the pressure of 37.5 psig at room temperature where the tests were carried out. Two bottles were treated at each temperature except for Example 6, where only one was treated. The results obtained are set forth in Table III below:

TABLE III

PERMEATION LOSSES OF FLUOROCARBON PROPELLANTS AT ROOM TEMPERATURE		
EXAMPLE	TREATMENT CONDITION	GRAMS LOST IN 5 DAYS
2	Not Treated	0.094 g, 0.107 g
3	25% F ₂ in N ₂ , 1 min. 60° C	0.0008 g, 0.004 g
4	25% F ₂ in N ₂ , 10 min. 65° C	0.0014 g, 0.0017 g
5	25% F ₂ in N ₂ , 1.5 min. 0.5 atm. pressure 65° C	0.007 g, 0.0017 g
6	50% F ₂ in N ₂ , 1.5 min 0.33 atm. 65° C	0.0023 g

Examples 3-6 show that 25% fluorine at pressures from 0.33 atm. to 1 atm. can be used in the apparatus to produce a useful change in the properties of the treated objects. In Examples 5 and 6, run at reduced pressure, no time was required after pressure equalization to pump up the reaction chamber. For these, the procedure was modified to eliminate the pump-up stage and the treatment time was lengthened from 1.0 to 1.5 minutes.

EXAMPLES 7 - 14

An additional series of experiments were performed using the apparatus and procedures employed in the previous examples. As in Example 1, one gallon high density polyethylene bottles were used. The treated bottles were also filled with about 2,800 grams of gasoline and the weight loss noted over a period of time. Different temperatures and pressures were used to demonstrate the utility of the apparatus at different conditions. In these examples, the apparatus was used with 10%, 25% and 50% F₂, at pressures from 1/2 atm to 1 atm, at room temperature and 66° C. Treatment time is the time at which the gas mixture is held in contact with the objects after the desired pressure is obtained and before the gas mixture is transferred back to the holding tank. The results are set forth in Table IV below.

TABLE IV

ROOM TEMPERATURE GASOLINE PERMEATION RESULTS					
EXAMPLE	Fluorination Conditions				Gasoline Wt. Loss (g) at 26 days
	% F ₂ Mix By Volume	Time	Temp.	Pressure	
7 (control)		Not Treated			-105 g
8 (control)		Not Treated			-106 g
9	10% F ₂ /N ₂	1 min.	RT	1 atm	- 37 g
10	25% F ₂ /N ₂	1 min.	RT	1 atm	- 21 g
11	25% F ₂ /N ₂	10 min.	66° C	1 atm	- 2 g
12	25% F ₂ /N ₂	1 min.	65° C	1 atm	- 3 g
13	25% F ₂ /N ₂	1 1/2 min.	65° C	1/2 atm	- 22 g
14	50% F ₂ /N ₂	1 1/2 min.	65° C	1/2 atm	- 12 g

EXAMPLE 15

A five gallon high density polyethylene drum was placed into the treatment chamber and treated with fluorine gas by the method employed in Example 1. The water jacket temperature was maintained at 62° C. and a fluorine concentration of 25 percent in nitrogen was employed. The treatment time was two minutes at one atmosphere. When the drum was removed from the treatment chamber, a slight dulling of surface gloss compared to that of an untreated drum showed that reaction with fluorine occurred.

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EXAMPLE 16

A commercially available wide mouth, eight ounce polycarbonate bottle was treated with fluorine by the method employed in Example 1. The water jacket temperature was maintained at 62° C and a fluorine concentration of 25 percent in nitrogen was employed. The treatment time was two minutes at one atmosphere. After removal from the treatment chamber, the treated bottle showed a slightly iridescent surface, displaying "interference colors", showing that the surface had reacted with fluorine.

EXAMPLE 17

Films of several different high and low density polyethylene material ranging in thickness from 1.1 to 1.7 mils and density from 0.915 to 0.96 gm/cm³ were clamped to a metal framework, placed in the chamber and treated according to the method of Example 1. The films were exposed to ten percent fluorine in nitrogen at 60° C for five minutes. Fluorination was evident from weight gains of the films of from 1 to 1.5 percent. Infrared spectral examination of the film also showed the appearance of absorption at approximately 1100-1200 cm⁻¹ due to the presence of C-F bonds.

EXAMPLE 18

Pieces of unfinished tanned leather—sheepskin, patent leather, boot leather, and dress shoe leather—were placed in the treatment chamber and treated by the method of Example 1, with the following specific conditions: 5% F₂ in N₂, 60° C jacket temperature, and 5 minute exposure time. Evidence of reaction noticeable on the samples removed from the reactor included curling, slight yellowing or discoloration and increased wettability when a drop of water was placed on the surface.

EXAMPLE 19

In order to demonstrate the use of the apparatus of this invention for halogenation with other than fluorine, a polyethylene bottle is treated with chlorine.

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Into a chamber with a well-sealable closure is placed a polyethylene bottle. By suitable means (vacuum pumps, refrigeration, etc.) the chamber is evacuated to 1 Torr. Cl_2 is allowed to flow into the reaction chamber through suitable connecting piping and valves from a holding chamber containing Cl_2 gas. Stainless steel or nickel and high nickel alloys such as Monel metal or Hastelloy are preferred for construction. Enough of the remaining Cl_2 in the holding tank is pumped into the reaction chamber which is maintained at 100°C to attain two atmospheres pressure. Optionally, a UV light illuminates the polyethylene bottles to initiate chlorination. After 10 minutes exposure, the unreacted chlorine and by-product HCl are permitted to flow to and then are pumped to the holding chamber via a scrubbing system containing KMnO_4 to absorb HCl and P_2O_5 to absorb H_2O . The reaction tank is flushed with dry nitrogen (exhausting to an aqueous NaOH scrubber) to absorb residual gases, pumped out once again if desired, filled with air, opened and the chlorinated objects removed.

EXAMPLE 20

In order to demonstrate that the apparatus of this invention is useful for treating objects with sulfur trioxide the following experiment is conducted.

Into a chamber at 60°C . with a closure is placed a polyethylene bottle. By suitable means (vacuum pumps, refrigerator, etc.) the chamber is evacuated to 1 Torr. Nitrogen containing 20% SO_3 gas is allowed to flow into the reaction chamber through suitable connecting piping and valves from a heated holding tank containing the N_2 , SO_3 mixture. Stainless steel or nickel and high nickel alloys such as Monel metal, or in some cases, aluminized steel, are preferred for construction. Enough of the remaining SO_3/N_2 in the holding tank is pumped into the reaction chamber which is maintained at room temperature to attain 1 atmosphere pressure. After 10 minutes exposure, the unreacted SO_3 is permitted to flow to and then is pumped to the holding chamber via a scrubbing system containing CaSO_4 or MgSO_4 to absorb any H_2O present or introduced with the sample bottle. The reaction tank is flushed with dry nitrogen or air (exhausting to an aqueous NaOH scrubber) to absorb residual gases, pumped out once again if desired, filled with air, opened and the sulfonated objects removed.

Although the invention has been illustrated by the preceding examples, it is not to be construed as being

limited to the materials employed therein, but rather the invention is directed to the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

What is claimed is:

1. An apparatus for exposing articles to a gaseous fluid at an essentially predetermined composition wherein said fluid is comprised of or contains one or more components which are reactive with the surface of said articles, said apparatus comprised of in combination:

- a first sealed reaction chamber having sealable access means for the introduction and removal of said articles;
- a second sealed chamber having first conduit means connected to at least one source of said fluid and optional sealable access means for the introduction and removal of said articles, whereby said second chamber may optionally be utilized as only a holding chamber for said gaseous fluid or additionally as a second reaction chamber;
- a conduit system connecting said first and second chamber;
- vacuum producing transfer means and valve means operatively associated with said conduit system for selectively creating pressure differentials between said chambers, whereby each chamber may be evacuated or charged with said gaseous fluid, and fluids transferred back and forth between said chambers after the fluid treatment of said articles;
- said apparatus including pressure and temperature control means; and
- means operatively associated with said conduit system and adapted to separate out reaction by-products and contaminants.

2. The apparatus of claim 1 wherein said articles are hollow in configuration and said first reaction chamber has means which allows for the introduction of fluid only to the interior of said articles.

3. The apparatus of claim 1 wherein said transfer means is comprised of, in combination, a piston-type compressor and a Rootes-type blower.

4. The apparatus of claim 1 where in said transfer means is a liquid sealed pump using an inert liquid.

5. The apparatus of claim 1 wherein at least one of said chambers is equipped with means for monitoring the concentration of reactive components.

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DISCUSSION

A. IDENTIFICATION OF MATERIALS

Polyethylene is an olefinic polymer of general structure $(H_2C:CH_2)_n$ and its general acceptance for use in application areas where it may contact food or drugs for human consumption is well established. Such general acceptance is acknowledged by specific citings in Food and Drug Administration (FDA) Code of Federal Regulations such as, but not limited to, Title 21 sections 121-2501 and 121-2514.

Fluorine is a nonmetallic halogen element of atomic number 9 and atomic weight 18.998. It exists, under conditions of our use, as a pale yellow diatomic gas (F_2) and is of pungent odor. Fluorine is the most electronegative element and is highly reactive forming fluorides with all elements except helium, neon and argon. The hazards of fluorine as a gas are its high toxicity and its activity as a strong corrosive irritant along with its flammability. Gaseous fluorine has a tolerance level of 1 p.p.m. in air¹ and is, with the existence of these cited properties, used and accepted in the manufacture of food and drug contact appliances and materials, e.g. fluorocarbon polymers.

The free fluorine gas is not an integral part of the articles resultant of our process but rather, because of its cited reactivity, exists as a fluoride chemically bonded to the polyethylene material. All excess "free gas" is removed from the process system prior to removing the treated articles for use and/or further processing, e.g. sterilization.

Nitrogen gas is the only other ingredient in this process of surface modification and is used as an inert diluent for the fluorine gas.

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Typical concentrations for this gaseous treatment of polyethylene on a volume basis are (b) (4) for treatment of pressurized use containers and (b) (4) for non pressurized applications.

¹ Condensed Chemical Dictionary - Ninth Edition, Van Norstrand/Reinhold

fluorinated species is removed as a xylene soluble (see figures 4-6)

In addition to the aforementioned testing progressing to our most recent studies, we included examination of our material according to an existing regulation for perfluorocarbons. The regulation applicable to this completely fluorinated polymer, but not to our surface fluorinated polyethylene, is CFR 121-2555.

Our tests according to this regulation were purely investigational to establish comparison data to this FDA accepted fluorinated polymer.

Testing in the case of 121-2555 involved refluxing a given amount of material for 2 hour periods separately in the four solvents; distilled water, 50 percent ethanol and water, n-heptane, and ethyl acetate; with total extractives not to exceed 0.2 mg per square inch of material and total fluoride removed not to exceed 0.03 mg per square inch. The data in Table XIV show our partially fluorinated polyethylene to be strikingly close to meeting these criteria in the area of total extractables and to meet total removable fluoride limit. This is despite the fact that radically different processes are involved in the production of these two materials. We reiterate that we make no claim to having created a perfluorocarbon by our process but rather, we've made a technological advance in the area of surface character alteration.

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The thrust of this writing is to petition for a new regulation or amendment of an existing regulation specifically dealing with Surface Fluorinated Polyethylene. To this end we've performed still additional extraction studies according to FDA Guidelines for Chemistry and Technology Requirements of Indirect Food Additive Petitions, March, 1976 edition.

In this phase of testing we used fluorinated containers of similar sizes and resins as used in the three immediately aforementioned studies (i.e. CFR 121-2514, 121-2501, 121-2555) along with appropriate control containers. All samples were sterilized in each of their respective food simulating solvents (distilled water, 50% ethanol in water,

heptane, and 3% acetic acid) for the 2 hour period and at the ¹temperatures suggested. Separate samples were monitored at the end of this period and then after 72 hours at reduced temperature². Intervals of 24 hours were used for further monitoring to a period of 168 hours. Selected time periods are those suggested in the FDA guidelines cited, except in the cases where n-heptane is the solvent where the minimum suggested times are exceeded, enhancing that extraction's severity.

In this, as in the other testing procedures we'd done previously, fluoride ion was the extractant monitored in the solvents.

The data in table XV are the average equilibrium values of fluoride ion extractant at the time periods specified.

It should be noted in this table, that the extractable fluoride values listed when n-heptane is the extracting solvent are not divided by five (5) as suggested but are the actual average values found.

Examination of these data shows that most values for extractable fluoride in all solvents are essentially 1 ppm or less. The exceptions are with the irradiated-fluorinated aerosol type containers where water, 50% ethanol in water, or 3% acetic acid is used as the solvent. In this case, a maximum equilibrium value of approximately 2.3 ppm is yielded with distilled water as the solvent.

Further examination of this table shows that equilibrium extracted fluoride for all samples is reached by 72 hours. It should also be noted, from this table, that n-heptane is the solvent extracting the minimum amount of fluoride ion.

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Complete data for these tests are presented in tables XVI through XXIII. In these tables, of significance is the observation that the solvents extracting the largest fluoride amounts, (>1ppm) cited earlier, extract nearly their equilibrium values during the sterilization periods.

¹ Sterilization temperatures: Water-250°F, Acetic Acid-212°F, Ethanol/Water-160°F, Heptane-150°F

² Equilibrium temperature: All solvents-120°F

PROPOSED REGULATION

Title 21 - FOOD and DRUGS

CHAPTER 1- FOOD and DRUG ADMINISTRATION

Department of Health, Education, and Welfare

Subchapter B- Food and Food Products

Part 177 - Indirect Food Additives; POLYMERS

Subpart B - Substances for use as basic components of single and repeated use food contact surfaces.

FLUORINATED POLYETHYLENE-

The Commissioner of Food and Drugs, having evaluated the data in a petition (8B3394) filed by Union Carbide Corporation, Sterling Forest Research Center, Long Meadow Road, Tuxedo , New York 10987, and other relevant material, concludes that the food additive regulations should be amended as set forth below, to provide for the safe use of fluorinated polyethylene as articles intended for use in contact with foods.

Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec 409(c), 72 Stat. 1786; 21 U.S.C. 348 (c) (1) and under authority delegated to the Commissioner, (21 CFR 177) is amended by inserting in the list of substances a new regulation as follows;

§ _____ Polyethylene, Fluorinated

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food contact articles in accordance with the following prescribed conditions;

(a) Fluorinated Polyethylene food contact articles are produced when polyethylene articles are surface modified by action of fluorine gas in combination with other gases such as nitrogen as inert diluents with such action leaving the polymer's bulk unchanged.

Fluorine gas shall be used in concentrations not in excess of amounts necessary to achieve the intended technical effect in the food or drug contact article.

(b) Polyethylene articles shall be flu-

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PROPOSED REGULATION - (Cont.)

orinated from basic resins identified and defined in §177.1520 paragraph(a)(2) and paragraph (a)(3) and shall conform to the specifications of paragraph (c)(2-1) and paragraph (c)(3-1).

(c) The finished food contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of §176.170(c) of this chapter, yields fluoride ion not to exceed 5ppm calculated on the basis of the volume held by the food contact article when tested by the methods described in §177.1330(c).

(Note; In testing the finished food contact article, use a separate test sample for each extracting solvent.)

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RE: Petition No. 8B3394

SECTION H - Environmental Impact Analysis Report.
(Pursuant to 21 CFR 6.1)

1. Describe the proposed action.

It is proposed that the Food and Drug Administration amend 21 CFR 177 by inserting fluorinated polyethylene as approved usage food contact articles.

2. Discuss the probable impact of the action on the environment (including primary and secondary consequences).

The impact on the environment will be minimal. Polyolefins such as polyethylene have been used for many years as food contact articles and containers. Fluorinated materials such as tooth paste, teflon, and potable water have also seen such usage and are generally recognized as safe (GRAS).

The disposal of these materials has not presented any particular environmental problem. The proposed fluorinated polyethylene material will merely replace other usage and chemically similar products and will require no extraordinary measure for disposal. Thus, there will be no necessary alteration of current common disposal techniques for handling such waste.

3. Discuss the probable adverse environmental effects which cannot be avoided.

Applicant knows of no adverse environmental effects caused by the limited use of fluorinated polyethylene as food contact articles.

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4. Evaluate the alternatives to the proposed action.

Alternatives to the proposed action would be to continue the use of less technically and less economically acceptable products for such usage.

5. Describe the relationship between local short term uses of the environment with respect to the proposed action and the maintenance and enhancement of long term productivity.

The effect of the proposed action on the environment is believed to be so minimal and insignificant that it is impossible to measure such relationship.

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6. Describe the irreversible and irretrievable commitment of resources which would be involved in the proposed action should it be implemented.

Raw materials are synthetic organic chemicals used in the ordinary production of polyethylene and elemental fluorine.

Should the proposed action be implemented, raw materials and energy presently used to produce current less technically and economically acceptable products would be diverted to production of the proposed product.

7. Discuss the objections raised by other agencies, organizations, or individuals which are known to the applicant.

Union Carbide Corporation as applicant knows of no such objections.

8. If the proposed action should be taken prior to 90 days from the circulation of a draft environmental impact statement or 30 days from the filing of a final environmental statement, explain why.

It is the belief of Union Carbide that this requested amendment represents a minimal change especially in light of the testing cited in this petition and the GRAS separate and similar and approved usage of the materials of manufacture. Under 21 CFR 6.1 (c) an environmental impact statement will not be required for an amendment to an existing regulation unless the change is substantial.

9. Analyze whether the benefit to the public of the proposed action will outweigh the actions potential risks to the environment.

Applicant sees no present or potential risk to the environment by reason of the proposed action.

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United States Patent Office

2,811,468

Patented Oct. 29, 1957

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2,811,468

IMPERMEABLE POLYETHYLENE FILM AND CONTAINERS AND PROCESS OF MAKING SAME

Stephen P. Joffré, Little Falls, N. J., assignor to Shulton Inc., Clifton, N. J., a corporation of New Jersey

No Drawing. Application June 28, 1956,
Serial No. 594,342

16 Claims. (Cl. 117—95)

This invention relates to polyethylene film and containers and more particularly to polyethylene film suitable for use as a wrapping material for foodstuffs and other perishable materials and to containers for perfume compositions, synthetic aromatic chemicals, natural isolates (fractions derived from natural sources, such, for example, as aromatic woods, barks, branches, flowers and fruits), other materials which are deleteriously affected either by the escape of vapors from the interior of the container through the walls thereof or by entry of constituents of the surrounding atmosphere through the walls of the container into contact with its contents, mineral and vegetable oils, aromatic hydrocarbons, e. g., toluene, aerosols in which a pressurized gas, such as nitrous oxide or the Freons are used as the propellants, emulsions in which the oil phase is the continuous phase, etc. The expression "container" is used herein in a broad sense to include bottles, boxes, envelopes, and the like.

Polyethylene containers, particularly bottles, are widely used for storing and transporting perfume compositions containing synthetic aromatic materials, such as citrus oils, clove oils, eugenol, isoeugenol, ionones, orange oils, lemon oils, etc., and other materials. Examples of such containers are the flexible polyethylene bottles including the now popular polyethylene squeeze bottles and bottles made from filled polyethylene compositions, such, for example, as mixtures of polyethylene and pigments and/or fillers such as barium sulfate, metal powders, talc, clay, etc. The latter type of bottle, while lacking the flexibility of the former, like the former has the advantage of unbreakability, as contrasted with glass, lightness in weight and the other advantages of polyethylene.

It is known that polyethylene is chemically inert to perfume compositions and aromatic chemicals, e. g., it will not dissolve therein or react therewith. Nor are the individual constituents of perfume compositions adversely affected by contact with polyethylene. Yet when perfume compositions are packaged in polyethylene containers not only does a rapid change in the character of the perfume occur but also weight losses from the sealed containers are considerable. In addition, distortion of the container frequently occurs. These changes in the composition of the perfume and the consequent weight losses are due to escape of the light notes (the fugitive or more volatile constituents), and sometimes also the medium notes through the walls of the polyethylene container, i. e. polyethylene is permeable to the constituents present in the perfume and the solvent employed (usually alcohol), permitting their escape in vapor or gaseous form through the walls of the sealed polyethylene container.

It is well known that, in order to create a good fragrance, light, medium and heavy notes must be blended

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judiciously. It has been the uniform experience of the perfume industry that any well constituted odor containing these three phases becomes unbalanced after storage in a sealed polyethylene container, even though no liquid leakage takes place from the container. The lighter notes disappear far more rapidly than the medium notes and the medium notes permeate the polyethylene walls more rapidly than the heavy notes. After awhile the unequal rate of permeation throws the fragrance completely out of balance.

Polyethylene containers can not be used, as a practical matter, for the storage of mineral or vegetable oils or emulsions in which oil is the continuous phase, because such oils diffuse through the walls. Attempts to store aromatic hydrocarbons, such as toluene, in polyethylene containers has resulted in the collapse and distortion of such containers. Nor have polyethylene containers been found suitable for packaging aerosols in which a pressurized gas such as nitrous oxide or the Freons chlorofluoro methanes or ethanes) including Freon 114 (dichlorotetrafluoro ethane) is used as the propellant because such pressurized gases escape through the walls with consequent loss of pressure within the container.

Polyethylene film, because of its clarity, tensile strength, relatively low moisture permeability, ease of handling, heat sealing ability and property of transmitting ultra-violet light, permitting surface sterilization of material wrapped with such film by means of ultra-violet light, is an eminently satisfactory wrapping material for materials which are not deleteriously affected by atmospheric gases, such as oxygen, air, carbon dioxide, or which do not contain flavor or odor constituents which escape through the polyethylene. The use of polyethylene film for packaging foodstuffs and other perishable materials deleteriously affected by atmospheric gases has been discouraged, if not substantially completely avoided, because of the relatively high permeability of polyethylene to atmospheric gases, particularly air and oxygen which cause spoilage, including changes in odor, color and/or flavor. Likewise, the packaging of meats, cheese, cooked foods, dried fruits, etc., in polyethylene film wrappers, has frequently resulted in discoloration, rancidity and poor flavor of the packaged material.

Much research and effort have been devoted to improving polyethylene film and containers so that they are relatively impermeable, i. e., will minimize, if not completely prevent, the passage of atmospheric gases or escape of odor, flavor or other constituents therethrough. To the best of my knowledge and belief, prior to my invention all of these efforts have been fruitless. Actually researchers in this field have turned to developing different polymers, such, for example, as halogenated polyethylenes, including polymeric trifluorochloroethylene and copolymers of vinyl chloride and vinylidene chloride from which containers may be made by injection into a mold or by blowing into a mold, etc. However, containers made from such polymers either sacrifice the desirable flexibility characteristics of polyethylene, are prohibitively expensive, or are objectionable for other reasons.

In the case of wraps for foodstuffs and other perishable materials, development has proceeded along the direction of (1) laminated films in which one film which is a good gas or vapor barrier but lacking in other desirable characteristics is bonded to another film having the desired qualities, e. g., polyethylene bonded to cellophane; (2) coated films, e. g., films coated with waxes or resins, including the polyvinyls; and (3) special plastics, such as

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Saran (polyvinylidene chloride), Mylar (polyester), which, while substantially impermeable to gases, are difficult to handle, lack ultra-violet transmission necessary for the sterilization of the surface of goods packaged therein, e. g., fresh meat, generate static electricity when handled, lack heat-sealability, are excessively costly, etc.

It is among the objects of the present invention to provide a polyethylene film and/or container, which film and walls of which container are relatively impermeable to the passage of atmospheric gases therethrough, and this without sacrifice to the desirable properties of the polyethylene, such as its clarity, tensile strength, ability to transmit ultra-violet light, and heat-sealing ability.

It is another object of this invention to provide polyethylene containers which are of improved impermeability to the passage of gases or vapors through the walls thereof and which containers, in the case of flexible polyethylene containers, such as squeeze bottle, retain the flexibility and other desirable characteristics of polyethylene, i. e., the improvement in the impermeability of the container is without sacrifice to the other desirable properties of polyethylene.

It is still another object of this invention to provide a polyethylene wrap or container which minimizes, if not completely prevents, the loss of aromatic flavor constituents from foods like cheese packaged in such wraps or containers; such loss, it will be appreciated, not only reduces customer acceptance of the food item but can also lead to flavor contamination of other food items stored in proximity therewith.

Still another object of the present invention is to provide a process for producing such polyethylene films or containers of improved impermeability which process is relatively simple and economical to carry out.

Other objects and advantages of this invention will be apparent from the following detailed description thereof.

In accordance with this invention, polyethylene film and/or containers are fluorinated to produce fluorinated polyethylene film and/or container walls containing from 0.03% to 3.5%, preferably from 0.05% to 1.5% by weight of fluorine based on the weight of the polyethylene. Surprisingly, I have found that the formation of such fluorinated polyethylenes results in a polyethylene film and/or container which is of surprisingly improved impermeability, and this without sacrifice to the desirable properties of the polyethylene.

It is important that the fluorination be carried out so as to produce a fluorinated polyethylene containing from 0.03% to 3.5% by weight of fluorine, based on the weight of the polyethylene. The desired improvement in the impermeability of the polyethylene is obtained as long as it is reacted with the fluorine to form fluorinated polyethylene containing fluorine in the amounts above indicated. While the explanation for the improvement in impermeability is not fully understood, it is believed due to the replacement of some of the hydrogen atoms of the polyethylene with fluorine which form an electrical lattice-work to prevent passage therethrough of vapors and/or gases. It will be understood that the above explanation is advanced for the purpose of facilitating a better understanding of the invention and that this invention is not to be confined to or limited by the above explanation.

Fluorination of the polyethylene to an extent to introduce more than approximately 3.5% by weight of fluorine does not result in the desired improvement in the impermeability of the polyethylene and may deleteriously affect other desirable properties of the polyethylene, such as its tensile strength and clarity. On the other hand, the fluorination of polyethylene so as to introduce fluorine in amount less than 0.03% based on the weight of the polyethylene does not result in the desired improvement in the impermeability.

The polyethylene, such as bottles and film, subjected to fluorination may have a thickness of from 0.25 to

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250 mils; in the case of film the thickness is from 0.25 to 25 mils. All commercial polyethylenes employed for the production of containers or in the form of film may be fluorinated in accordance with this invention to render them substantially impermeable. Such polyethylene usually consists of polymers of ethylene having a molecular weight of at least 10,000, preferably from 14,000 to 60,000.

In the fluorination of the polyethylene film, the film should be free of lint and grease. This is preferably accomplished by washing the film with a low boiling grease removing solvent, such as carbon tetrachloride, acetone, ether or perchloroethylenes, to remove all grease, dust and foreign matter which, if not removed, might cause ignition of the polyethylene. Thereafter, the film is contacted with pure fluorine (100%) or a mixture of fluorine and an inert gas containing at least about 10% fluorine. The fluorination may be continuous by continuously passing the film through the fluorine or fluorine mixture maintained in a suitable sealed chamber provided with gas-tight seals through which the film enters and leaves. Alternatively a wound reel of the film can be unrolled and rerolled in the treatment chamber.

Instead of the continuous treatment hereinabove described, the treatment may be a batch operation involving festooning or otherwise arranging the clean film within the reactor to expose both sides, then introducing the fluorine or fluorine mixture into the reactor and permitting the film to remain in contact with the fluorine for the desired time interval. While not preferred, if desired the fluorination treatment may be carried out so that only one side of the film is fluorinated to form a layer of fluorinated polyethylene containing from 0.03% to 3.5%, preferably from 0.05% to 1.5% fluorine.

The time of treatment will depend on the particular equipment used, the film to be treated, the concentration of fluorine used, and the temperature. In general, a treatment time (contact time between the polyethylene and the fluorine) of from about 5 minutes to about 3 hours will give satisfactory results at room temperature (20°-25° C.). It is preferred to operate at room temperature, although temperatures as high as 50° C. may be employed. The more concentrated the fluorine atmosphere, the shorter the treatment time. Also, elevating the temperature to not exceeding 50° C. will permit shortening the treatment time. In the case of films in the lower portion of the 0.25 to 25 mils thickness range, it is preferred to use a relatively short treatment time. Treatment times exceeding 3 hours may be used but are not preferred because they do not result in material further improvement in the impermeability of the polyethylene.

Following the above noted conditions, it has been found the film is not charred nor is there any material loss of clarity or tensile strength; the impermeability of the film to gases is, however, greatly improved as will be evident from the test data given below.

The fluorination of polyethylene containers is carried out by first cleaning each container so that it is free from lint and oil, introducing the clean container into a chamber, evacuating this chamber, then introducing fluorine gas into this chamber and continuing this introduction to the desired extent. Maintenance of each container in the chamber in contact with the fluorine gas for from 20 to 150 minutes usually suffices to produce the desired level of fluorination. Thereafter, the container is removed from the chamber and its interior and exterior flushed with air or other inert gas, such as nitrogen, to remove residual fluorine gas.

In lieu of the above procedure, each container after cleaning, as above described, may be introduced into an atmosphere of fluorine gas and maintained therein for a sufficient period of time, say from 10 to 45 minutes, to effect the fluorination of the polyethylene.

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The time of treatment of the containers will depend on the equipment used, the containers to be treated, the concentration of fluorine used and the temperature. At atmospheric temperature, a treatment time of from 5 minutes to 3 hours will give satisfactory results. Elevating the temperature or using more concentrated fluorine atmospheres, or both, will permit the use of shorter treatment times. Treatment times exceeding 3 hours may be employed but are not preferred because they do not result in further improvement in the impermeability of the polyethylene. Excessively long treatment times should not be used because they adversely affect the tensile strength of the polyethylene.

The cleaning of the containers before they are subjected to fluorination is desirably effected by washing the container with a suitable solvent for oil or grease, such as carbon tetrachloride, acetone, ether or perchloroethylene, and thereafter removing residual traces of the solvent, for example, by blowing clean air over and through the washed containers. Unless the containers are clean when subjected to fluorination, particularly at temperatures above room temperature, there is the danger that when the container is fluorinated the polyethylene will ignite. By observing the conditions hereinabove set forth, namely, at temperatures below 50° C., preferably at room temperature, and utilizing clean containers, particularly in that they are free of lint and oil or grease, this danger is eliminated.

While it is preferred to fluorinate both the interior and exterior of the container, as hereinabove described, only the interior or only the exterior of the container may be so treated and still obtain the desired improvement in the impermeability of the walls of the container.

In all modifications, including the fluorination of polyethylene film, instead of an atmosphere containing 100% fluorine, the fluorine may be diluted with an inert gas. The fluorine concentration may vary from 2% to 100% by weight, the balance, if any, being the inert gas, such as nitrogen, air, Freon (chlorofluoro alkanes, e. g., methanes and ethanes), etc. When a diluted fluorine is used, it is important to dry the diluent, i. e., substantially anhydrous conditions should be maintained during the fluorination. The presence of moisture tends to result in undesirable side reactions with the fluorine.

While the fluorination desirably is carried out at room temperature (20°-25° C.) any desired temperature below 50° C. may be used.

The following comparative data shows the surprising improvement in impermeability of polyethylene films and containers effected by the present invention.

CONTAINERS

In all of the container examples, flexible bottles were employed made of a commercial polyethylene having an average molecular weight of 21,000; the bottles were oval shaped and the walls thereof varied in thickness from 20 to 60 mils.

Example I

Pre-formed clean polyethylene bottles, each of 5 3/4 oz. capacity, were treated with a stream of fluorine gas at room temperature (20°-25° C.) for six hours and for twelve hours. A 1 cm. diameter punch taken from the thickest aspect of the bottle wall from bottles which were fluorinated for 6 hours contained approximately 0.3% fluorine. The bottles fluorinated for 12 hours contained approximately 1.5% fluorine. The bottles were then flushed with air until no residual odor remained and filled to capacity with liquid allyl caproate and then sealed. This material was used as a test liquid because of its high volatility and distinctive odor and also because it has been found to be an excellent medium for indicating the permeability characteristics of polyethylene.

The filled bottles were then weighed, stored on open

shelves at room temperature for the periods indicated in the table which follows and at the termination of each of these periods the bottles again weighed and the gross losses in weight noted. An identical, fluorine untreated bottle was subjected to the same test for control purposes. The data on this test is given in Table 1 which follows:

TABLE 1

Bottle Type	Percent Loss in Gross Weight		
	10 days	21 days	40 days
(a) Untreated bottle.....	0.8	2.42	5.67
(b) 6 hr. fluorine treatment.....	0.0009	0.007	0.0512
(c) 12 hr. fluorine treatment.....	0.020	0.104	0.400

From the above data, it will be noted the untreated bottle lost at the end of 40 days 100 times more weight than the bottle treated for 6 hours. The strong characteristic odor of allyl caproate was readily detectable from the untreated bottle whereas it was not noticeable from the outer walls of the treated bottles.

Example II

Clean polyethylene bottles of 5 3/4 oz. capacity were fluorinated by passing a stream of gas from the inside of one bottle to the inside of the next bottle, the bottles being connected with fluorine resistant tubing. The bottles were treated with a stream of fluorine at room temperature for different periods of time indicated in the table which follows, thus introducing varying amounts of fluorine from 0.05% to 3.5% by weight. At the end of the fluorination the bottles were flushed with air until no residual odor remained, filled to capacity with liquid allyl caproate, and sealed. A control bottle was similarly filled to capacity with the same test liquid and sealed. The sealed bottles were weighed, stored on open shelves at room temperature for 40 days, thereafter again weighed and the gross loss in weight noted. The data on this test is given in Table 2 which follows:

TABLE 2

Bottle	Time of Treatment, hours	Percent Gross Loss in Weight
Control (untreated).....	None	4.0
Treated.....	1/2	0.00174
Do.....	1	0.00224
Do.....	2	0.00199
Do.....	3	0.00542
Do.....	4	0.00293

During and at the end of the test, the strong characteristic odor of allyl caproate was readily detected from the untreated bottle, whereas the outer walls of the treated bottles did not have any noticeable odor.

Example III

The polyethylene bottles were first thoroughly cleaned to remove lint, oil and grease and then were placed in a chamber at room temperature. The air was evacuated from this chamber. Fluorine gas was slowly fed into the chamber so that at the end of an hour atmospheric pressure was established in the chamber. The fluorine gas was then permitted to remain in contact with the polyethylene bottles for another hour and thereafter the entire system was flushed with air until no residual odors remained.

Bottles thus treated were then filled with (a) the test liquid allyl caproate, (b) with a fragrance sold commercially under the trade name of "Desert Flower Toilet Water" and (c) with a lotion sold commercially under the trade name of "Old Spice After-Shave Lotion." The bottles were weighed, stored on open shelves at room temperature, again weighed at the end of the test period indicated in the table which follows, and the gross loss in weight noted. Untreated polyethylene bottles were subjected to the same

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treatment for control purposes. The data obtained on this test is given in Table 3 which follows:

TABLE 3

Bottle	Total Treatment Time, hours	Test Liquid	Duration of Test, days	Percent Gross Loss in Weight, average
Control.....	None	Allyl Caproate.....	40	2.9
Treated.....	2	do.....	40	0.053
Control.....	None	Old Spice After-Shave.....	27	0.26
Treated.....	2	do.....	27	0.06
Control.....	None	Desert Flower Toilet Water.....	40	0.30
Treated.....	2	do.....	40	0.11

During and at the end of the test period the strong characteristic odor of allyl caproate and Desert Flower Toilet Water was readily detected from the outer walls of the untreated bottles (the control bottles) whereas there was no noticeable odor of the test liquids on the outer walls of the treated bottles. Likewise, the untreated bottles containing Old Spice After-Shave Lotion had a faint spice odor on their outer walls, while this was not noticeable with the treated ones.

In Table 3-A below is given the concentration of fluorine and the diluent used in treating polyethylene bottles made from polyethylene having an average molecular weight of 21,000 to 23,000; this table also gives the fluorine content and treatment times of the resultant bottles.

TABLE 3-A

Fluorine Concentration, percent by volume		Treatment Time, Minutes	Percent F by weight
F	Nitrogen		
32	68	30	0.18
53	47	90	0.68
3	97	30	0.09
15	--	30	0.81
100	--	90	0.19
100	--	90	0.12
85	15	30	0.12
85	15	60	0.13
85	15	120	0.15

¹ In this example, the bottles were placed in a closed chamber, the chamber sealed and evacuated and an amount of fluorine introduced into the chamber equal to 5-- of the volume of the chamber.

FILMS

All film permeability data hereinafter given was obtained using the apparatus and the test procedure described in the article by A. Cornwell Sherman, entitled "Apparatus for measuring the gas permeability of film materials of low permeability," published in "Industrial and Engineering Chemistry," Analytical Edition, vol. 16 (No. 1), pages 58 through 60, January 15, 1944.

Example IV

In the film examples, the molecular weight of the polyethylene was about 23,000.

25 ft. of polyethylene film, 8 inches wide and 1.2 mils in thickness were washed with carbon tetrachloride to remove oily residues and foreign matter. The film was then air dried and festooned in the gas-tight treatment chamber to expose both sides of the film. The chamber was then evacuated and filled with dry nitrogen. This evacuation and filling process was twice repeated in order to flush the treatment chamber of any initial undried moisture-bearing atmospheric air. The treatment chamber, after this flushing, was evacuated to approximately 28 inches of vacuum and then filled with fluorine gas, over a 30 to 40 minute time interval until the vacuum was about 14 inches. At this point, the flow of fluorine gas into the chamber was stopped and dry nitro-

gen gas was introduced into the chamber until the pressure was one atmosphere. The treatment chamber then contained 50% fluorine gas and 50% nitrogen.

The polyethylene film was permitted to remain in the treatment chamber for 30 minutes and thereafter the chamber was flushed with dry nitrogen to remove substantially all of the fluorine gas. The chamber was then opened, the film removed, washed with cold tap water, air dried and stored for 48 hours in an air conditioned room having a relative humidity of 45-50% and at a temperature of 76-78° F.

The resultant film was clear and showed no reduction in tensile strength. The film before and after treatment was tested to determine its permeability to oxygen and carbon dioxide with the following results:

OXYGEN PERMEABILITY

Film before treatment 303
Film after treatment 46

CARBON DIOXIDE PERMEABILITY

Film before treatment 995
Film after treatment 148

The above values and all permeability values herein after given are in terms of the number of cubic centimeters of the particular gas under test transmitted per hundred square inches of film surface per 24 hours.

Example V

30 Sheets of polyethylene film 8" wide, 10" long, and 2 mils in thickness, were washed with carbon tetrachloride to remove any oily residues and foreign matter. The film was air dried and placed in the gas-tight treatment chamber, which was flushed with dried air. The treatment chamber was then filled with a mixture of 50% by volume fluorine gas and 50% by volume of dried air and the film permitted to remain in this mixture for 30 minutes. The chamber was then flushed with dried air to remove substantially all of the fluorine gas. The chamber was then opened to the atmosphere; the film removed, washed with cold water, dried in air, and then stored for 48 hours in an air conditioned room, as in Example IV.

Tests on this film before and after treatment, to determine air and Freon 114 (dichloro-tetrafluoro ethane) permeability, gave the following results:

AIR PERMEABILITY

Film before treatment 135
Film after treatment 67

FREON 114 PERMEABILITY

Film before treatment 138
Film after treatment 25

Example VI

A sheet of polyethylene film 8" wide, 12' long, and 5 mils in thickness, was washed with acetone to remove any oily residues and foreign matter, then air dried, and placed in the gas-tight treatment chamber, which was thereafter flushed with dried air. The treatment chamber was then filled with a mixture of fluorine and dried air so as to contain 40% fluorine by volume. The film remained in this atmosphere within the treatment chamber for 10 hours. Thereafter, the treatment chamber was flushed with dried air to remove substantially all of the fluorine. The film was thereafter removed from the chamber, washed in cold tap water and dried. It was then tested for oxygen permeability, with the following results:

Film before treatment 90
Film after treatment 28

In Table 4, which follows, there are given the permeability values for different thicknesses of film, before and after treatment, subjected to fluorination treatment, using

the difference chamber. The fluorine was the same. Example

Film Thickness, Mils

2.5
2.0
1.3
1.0

2.0
1.3
1.0
2.5

2.0

¹ Air in a

In all the treated film, the sealing was violet light and untreated 230 to 2 little or with this comparison transmittance length of gradually approximate wave length film show lengths of

The treated film printed on polyethylene was found the scotch tape printing

The in have all the case fluorinated flexibility

In the bottles, the deleterious ethylene, or other bottles

be found storage of deodorant

The permeability container such as dioxide, serving as a bleaching agent

the different concentrations of fluorine in the treatment chamber, and the time of treatment indicated in the table. The fluorination procedure otherwise was substantially the same as hereinabove described in connection with Example IV.

TABLE 4
OXYGEN PERMEABILITY

Film Thickness, Mils	Percent by Volume Fluorine and Diluent Concentration in Treatment Chamber		Duration of Treatment in Hours	Permeability of Film Before Treatment	Permeability of Film After Treatment	Percent Reduction in Permeability Effectuated by Treatment
	F	Diluent				
2.5.....	85	15 air	2	116	23	78.5
2.0.....	85	15 air	1	167	39	76.4
1.3.....	50	50 N ₂	1/2	256	44	82.7
1.0.....	50	50 N ₂	1/2	303	46	84.8

CARBON DIOXIDE PERMEABILITY

2.0.....	85	15 air	1	600	136	77.2
1.3.....	50	50 N ₂	1/2	995	148	85.2
1.0.....	50	50 N ₂	1/2	814	122	85.0
2.5.....	10	90 Air	1	406	161	60.2

FREON 114 PERMEABILITY

2.0.....	50	50 Air	1/2	138	25	81.9
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¹ Air in all examples was dried air.

In all of the above examples, the fluorinated polyethylene retained its original tensile strength, clarity, heat-sealing ability, and its property of transmitting ultra-violet light. The percentage transmittance of the treated and untreated polyethylene film for wave lengths of from 230 to 280 millimicrons (the ultra-violet range) shows little or no difference for film fluorinated in accordance with this invention and for the untreated film. In one comparative test the fluorinated film showed a percentage transmittance of about 28% for radiation having a wave length of 230 millimicrons, the percentage transmittance gradually increasing with increase in the wave length to approximately 70% in the case of radiation having a wave length of about 380 millimicrons. The untreated film showed a transmittance in this same range of wave lengths of only 1% or 2% greater than the treated film.

The treated film takes print much better than the untreated film. Thus, for example, when untreated film was printed using inks specially prepared for printing on polyethylene and scotch tape applied over the printed area, it was found that the printing could readily be removed with the scotch tape, in the case of untreated film, but the scotch tape remained clear, i. e., would not remove the printing in the case of the treated film.

The impermeable containers embodying this invention have all the desirable properties of the polyethylene; in the case of flexible bottles, such as squeeze bottles, the fluorination treatment does not deleteriously affect the flexibility of the polyethylene.

In the case of the more rigid type of polyethylene bottles, the treatment of this invention does not have any deleterious effect on the desirable properties of the polyethylene, i. e., does not cause substantial rigidification or otherwise deleteriously affect the polyethylene.

Bottles treated in accordance with this invention will be found eminently satisfactory for the packaging and storage of toilet waters, cosmetic lotions, colognes, liquid deodorants, etc.

The present invention provides polyethylene film and containers which are substantially impermeable to gases, such as oxygen, air, nitrogen, nitrous oxide, carbon dioxide, the Freons, sulfur dioxide, ethylene, other preserving or pressurizing gases or fluids, and to the vaporizable constituents, including the light and medium notes

of perfume compositions, and this without sacrifice to the flexibility, heat sealability and ultra-violet light transmitting properties of the polyethylene.

Films embodying this invention provide an excellent wrapping material for foodstuffs and other perishable materials deleteriously affected by atmospheric gases.

Films embodying this invention may be formed into a bag to provide a membrane in an aerosol package, separating Freon, nitrous oxide or other gaseous propellants from the foodstuff or other material placed in the bag within the aerosol package. For example, anchovy paste, mayonnaise, jams, etc., may be packaged in such fluorinated polyethylene bags disposed in a suitable container, such as a metal container having a Freon or other gaseous propellant, the polyethylene bag serving to maintain the foodstuff out of contact with the gaseous propellant, while the foodstuff is within the container. In this way, the foodstuff may be dispensed in the form of a ribbon or controlled stream from the container by releasing the pressure, and this without intermingling of the foodstuff with the propellant.

Moreover, the present invention provides a substantially impermeable container which may be used in storing or packaging toluene, other aromatic solvents, mineral oils, including refined petroleum oils, vegetable oils, such as corn oil, peanut oil, cottonseed oil, and emulsions in which oil is the continuous phase, providing an unbreakable container in which the flexible properties of the polyethylene may be utilized, e. g., a squeeze bottle for storing and dispensing such oils, emulsions, etc. Hence, polyethylene bottles embodying this invention may be used as squeeze bottles for storing and dispensing as a spray such oils and oil emulsions.

In this specification, unless otherwise indicated, percentages are on a weight basis. The pressures hereinabove given are in terms of inches of mercury. The expression polyethylene, it will be understood, includes the polymethylenes which are produced by the polymerization of ethylene.

This application is a continuation-in-part of copending application Serial No. 492,030, filed March 3, 1955, which application (but not the invention thereof) has been abandoned in favor of this application.

Since certain changes in carrying out the process and in the containers embodying this invention may be made without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense. Thus, instead of using gaseous fluorine for the fluorination treatment, a solution of fluorine in a suitable solvent may be employed.

What is claimed is:

1. A polyethylene film having at least one surface fluorinated, to contain not more than about 3.5% by weight of fluorine and enough fluorine so that said surface is substantially impermeable to the passage of atmospheric gases therethrough.
2. A polyethylene film containing from 0.03% to 1.5% by weight of fluorine.
3. A polyethylene container having its walls fluorinated, to contain not more than about 3.5% by weight of fluorine and enough fluorine so that the walls of said container are substantially impermeable to the passage therethrough of the light notes of perfume compositions.
4. A polyethylene container having its walls fluorinated to contain less than about 3.5% by weight of fluorine and enough fluorine to render the walls substantially impermeable to the passage therethrough of the light notes of a perfume composition.
5. A polyethylene container having fluorinated polyethylene walls containing from 0.03% to 3.5% by weight of fluorine.
6. A polyethylene container having a wall thickness of from 0.25 to 250 mils and having fluorinated poly-

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ethylene walls containing from 0.03% to 3.5% by weight of fluorine.

7. A polyethylene container having a wall thickness of from 0.25 to 10 mils and having fluorinated polyethylene walls containing from 0.05% to 1.5% by weight of fluorine.

8. A polyethylene container constituted of polyethylene having a molecular weight of from 14,000 to 60,000, a wall thickness of from 0.25 to 250 mils and having fluorinated polyethylene walls containing from 0.03% to 3.5% by weight of fluorine.

9. A container of polyethylene having a molecular weight of from 14,000 to 60,000, a wall thickness of from 0.25 to 250 mils and having the walls fluorinated to contain from 0.03% to 3.5% by weight of fluorine based on the weight of the polyethylene.

10. A process of fluorinating a wall constituted of polyethylene to render it substantially impermeable to the passage therethrough of aromatic flavor constituents which comprises fluorinating the said wall to contain not more than about 3.5% by weight of fluorine to render the polyethylene substantially impermeable to the passage therethrough of said aromatic flavor constituents.

11. A process of fluorinating a polyethylene surface adapted to form a container which comprises contacting said polyethylene surface with fluorine to form a fluorinated polyethylene surface containing from 0.03% to 3.5% by weight of fluorine.

12. A process of fluorinating polyethylene film which comprises cleaning the film to remove grease and foreign matter therefrom, subjecting the cleaned polyethylene film to contact with fluorine gas for from 5 minutes to 3 hours to fluorinate said polyethylene to a maximum of 3.5% by weight of fluorine, and flushing said polyethylene with a gas to remove residual fluorine therefrom.

13. A process of treating polyethylene containers which process comprises fluorinating the walls of said containers to introduce from 0.03% to 3.5% of fluorine based on the weight of the polyethylene walls.

14. A process of treating polyethylene containers which

process comprises cleaning the containers to remove lint and oil therefrom, passing fluorine into contact with the walls of said containers while maintaining said walls at a temperature below 50° C. and continuing said passage of fluorine into contact with the walls of said containers until the polyethylene walls contain from 0.03% to 3.5% by weight of fluorine based on the weight of the polyethylene, discontinuing passage of the fluorine into contact with the walls of said polyethylene containers and flushing the walls with an inert gas to remove unreacted fluorine therefrom.

15. A process of treating polyethylene containers, which process comprises cleaning the interior and exterior walls of the container to remove lint and oil therefrom, introducing the clean container into a chamber, evacuating said chamber, introducing fluorine into said chamber into contact with the interior and exterior walls of said container, maintaining said container in contact with the fluorine until the polyethylene walls of the container contain from 0.03% to 3.5% by weight of fluorine, removing the container from the chamber and flushing the walls of the container with an inert gas to remove unreacted fluorine.

16. The process as defined in claim 15, in which the temperature of the container while in contact with the fluorine is maintained below 50° C.

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2,502,841	Henderson	Apr. 4, 1950

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Endgroups in Tetrafluoroethylene Polymers*

M. I. BRO and C. A. SPERATI, *Polychemicals Department,
E. I. du Pont de Nemours & Co., Inc., Du Pont
Experimental Station, Wilmington, Delaware*

INTRODUCTION

In 1951, Berry and Peterson¹ polymerized tetrafluoroethylene in an aqueous system using radioactive persulfate ($K_2S_2O_8$) as the initiating agent. The resulting polymer was inactive. It was suggested at that time that the initiating species was a sulfate ion radical and that the resulting perfluoropalkyl sulfuric ester hydrolyzed immediately with water to produce a carboxyl endgroup. It was also suggested that hydroxyl radicals formed from the interaction of sulfate ion radicals and water might initiate the polymerization, and that the resulting perfluoroalcohol hydrolyzed immediately to the acid.

During the course of our research, we had occasion to prepare a number of these polymers under generally similar conditions using ammonium persulfate $[(NH_4)_2S_2O_8]$ initiator. In this paper, we report experimental evidence which indicates that the ends are carboxyl groups when the polymerization is carried out in the presence of water.

EXPERIMENTAL

Polymerization

Platinum-lined pressure vessels of 330 ml. capacity were charged (under nitrogen) with 200 ml. of distilled water containing the desired amount of initiator (Table II). The vessels were placed in a shaking apparatus behind a suitable barricade, evacuated, and brought to reaction temperature. Purified tetrafluoroethylene was charged to attain a pressure of about 100 p.s.i. The polymerization temperature was measured using an iron-Constantan thermocouple placed in a well set deeply into the vessels and controlled automatically within $1^\circ C$. by a Micromax controller. The rate of shaking was constant throughout all runs. The vessel was repressured to 100 p.s.i. with additional tetrafluoroethylene from time to time when the pressure dropped below 50 p.s.i. The reaction was continued until sufficient polymer was obtained for our studies.

* This research was presented at the 135th National Meeting of the American Chemical Society in San Francisco, April 1958. Cf. abstract p. 22R

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M. I. BRO AND C. A. SPERATI

Isolation of Polymer

The polymers as removed from the pressure vessel were either water wet or nonwater wet white granules, which were freed from the polymerization liquors by filtration on coarse grade sintered-glass funnels. The polymers were then stirred mechanically in 20% HCl (Samples 3 and 4) or 20% H₂SO₄ (Samples 1 and 2) for several hours with a stirring blade fabricated from Teflon* TFE-fluorocarbon resin. This was followed by repeated washings with distilled demineralized water and continuous extraction with acetone (five days). The samples were then dried at reduced pressures for 24 hours at 55°C.

Neutralization

Polytetrafluoroethylene is insoluble in all solvents at ordinary temperatures. However, it is wetted by water-ethanol mixtures. Weighed samples (3 to 5 g.) were placed in beakers (under an atmosphere of nitrogen) containing 100 ml. of absolute ethanol and 100 ml. of distilled water. The suspended polymers, which were well wetted by this solution, were carefully titrated to pH 7 with 0.01 N NaOH. A total of seven hours was required for these neutralizations. The titrated samples were filtered on sintered-glass funnels and dried at 55°C. at reduced pressures.

Pyrolysis

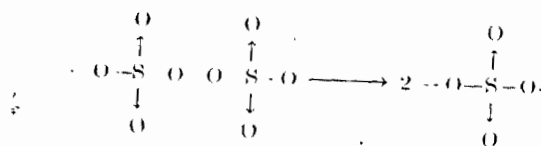
Two to three gram portions of the neutralized and dried samples were placed in 125 ml. round-bottom flasks, and heated at 300°C. from one-half to three hours in the absence of air and then allowed to cool to room temperature. The sample in Experiment 3 was heated only one-half hour.

Infrared Spectroscopy

The dried polymer was cold pressed into thin films in a Preco Press. The films were scanned in the region of 2 to 8 μ in a Perkin-Elmer Model 21 infrared spectrophotometer using a calcium fluoride prism. The absorption bands of interest were calibrated against those observed in model compounds of known structure (examples: perfluorobutyric and perfluorooctanoic acids, their sodium salts, and perfluoroheptene-1 and perfluorononene-1, as shown in Table I).

DISCUSSION

In alkaline, neutral, or slightly acidic (above pH 2.5) solutions, persulfate decomposes by a symmetrical rupture of the $-\text{O}-\text{O}-$ link to form two identical free radicals:²



* Du Pont registered trademark.

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TABLE I
Infrared Absorption Bands of Selected Fluorocarbon Compounds

Compound	Infrared absorption maxima μ			
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_3\text{F}_7\text{C}-\text{OH} \end{array}$	2.79	3.24	5.52	5.62
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_7\text{F}_{15}\text{C}-\text{OH} \end{array}$	2.80	3.24	5.52	5.62
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_3\text{F}_7\text{C}-\text{ONa} \end{array}$		5.90		
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_7\text{F}_{15}\text{C}-\text{ONa} \end{array}$		5.90		
$\text{C}_6\text{F}_{11}\text{CF}=\text{CF}_2$		5.58		
$\text{C}_7\text{F}_{13}\text{CF}=\text{CF}_2$		5.58		

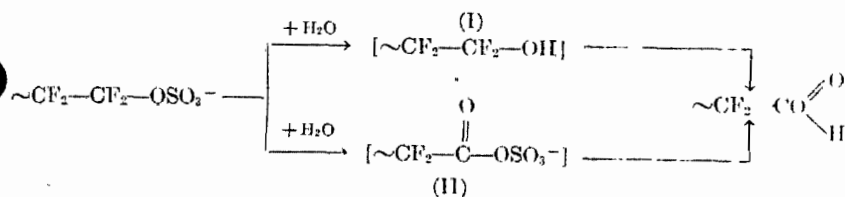
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U. S. PATENT OFFICE

In the presence of tetrafluoroethylene, the sulfate ion radical reacts with monomer to initiate polymerization. Thus, providing no chain transfer occurs, at least one end of each polymer chain bears a $\text{CF}_2\text{CF}_2\text{—OSO}_3\text{—}$ group. If termination is by combination of two growing chains or a growing chain and an initiator radical, both ends of the chain should bear these groups.

The perfluoroalkyl sulfuric ester hydrolyzes to a long chain perfluoroalkyl carboxylic acid by one of the following routes.



Intermediate (I) is the unstable perfluorocarinol structure which hydrolyzes very quickly to the acid.³ The intermediate (II) also hydrolyzes rapidly. Lower homologs of this type react vigorously with cold water.⁴ Fluoride ion was noted in the polymerization liquors, but it is also known that monomer itself hydrolyzes to a small extent.

While no hydrogen ion catalysis would be expected under the conditions of our experiments (pH 3 to 4), those radicals which did not initiate a chain would be expected to form hydroxyl radicals.

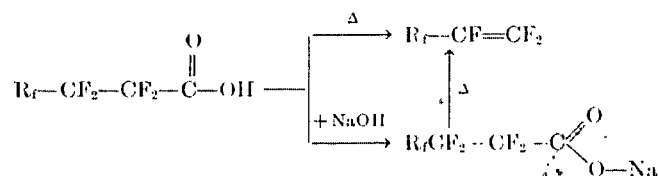


This radical would also initiate polymerization, forming again the unstable 1,1-difluorocarinol structure described above which hydrolyzes in water to the carboxylic acid.

Perfluorocarboxylic acids can be pyrolyzed to an olefin with one less carbon,⁵ and their dry alkali metal salts behave similarly.⁶

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Typical infrared scans of these compounds are shown in Figure 1.

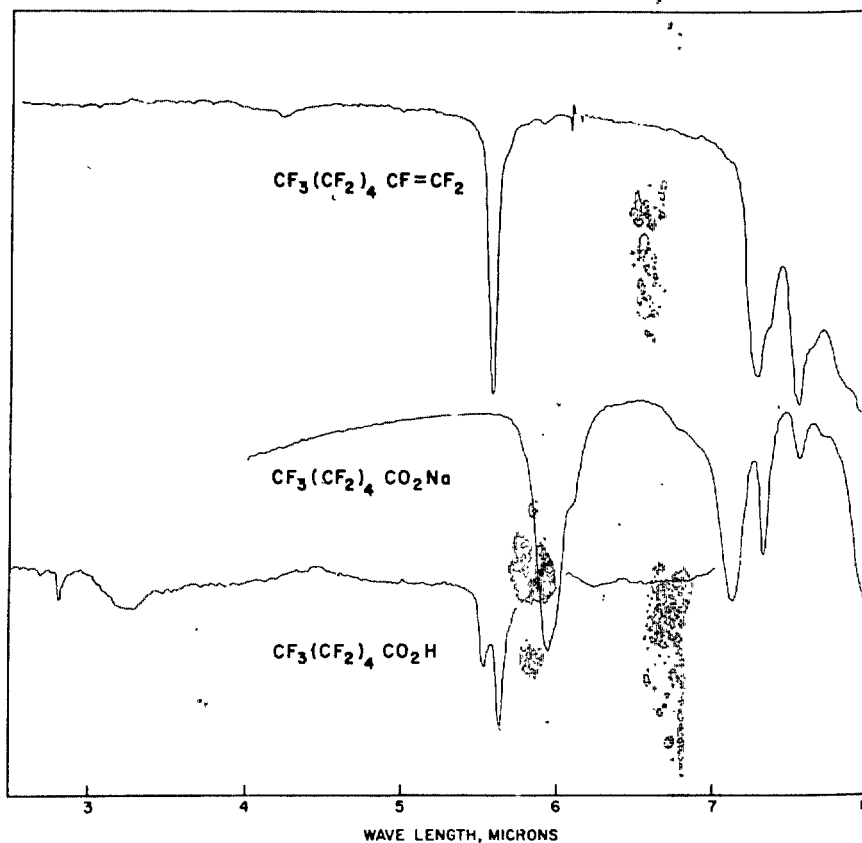


Fig. 1. Infrared spectra of fluorocarbon derivatives.

Similar reactions should be expected in high polymers containing such endgroups; in our experiments these changes were followed by observing the differences in the infrared absorption band spectra of the various products.^{7,8} The acidified, washed, and dried products were cold pressed into thin films and examined in the infrared. As can be seen in Figure 2 (bottom scan) strong absorption bands were observed at 5.52 and 5.62 μ which are typical of COOH in fluorocarbons, as well as peaks in the region of 2.80 and 3.24 microns. After titration of the polymer in ethanol-water mixtures with sodium hydroxide (followed by drying), the samples showed a decrease in absorption at 5.52 and 5.62 μ , accompanied by the appearance

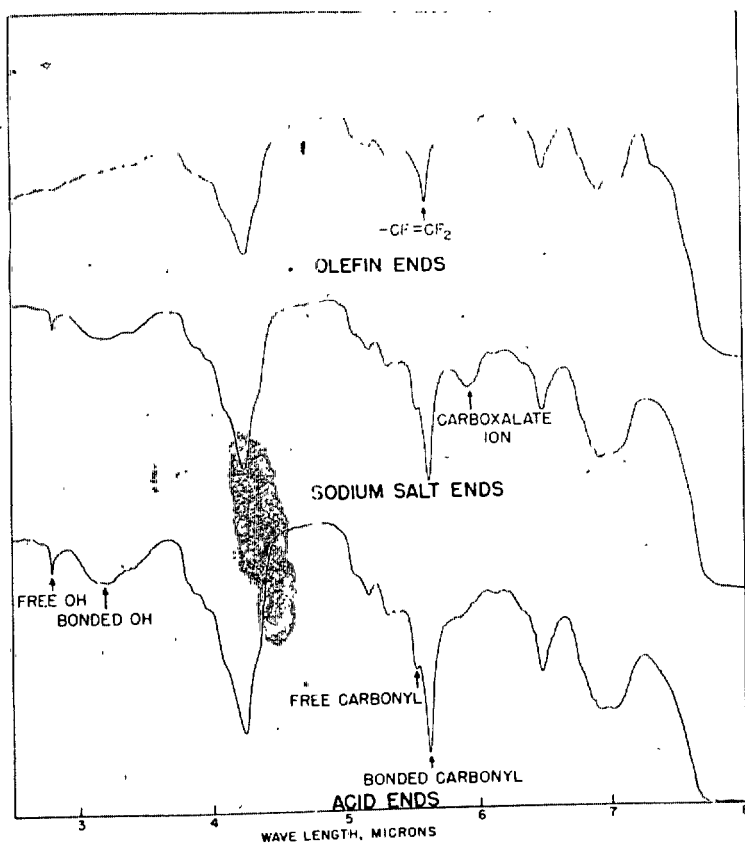


Fig. 2. Infrared spectra of polytetrafluoroethylenes.

strong bands at 5.93μ characteristic of $\text{C}=\text{O}$ in fluorocarbons, as shown in the middle scan of Figure 2. Pyrolysis of the dried sodium salt in the absence of air gave a decarboxylated product that was completely free of absorption in the regions of 2.81, 3.2, 5.52, and 5.62. However, a new band appeared at 5.60, (top scan) which is assigned to the terminal $\sim\text{CF}=\text{CF}_2$ group. The results of four such experiments are presented in Table II.

The presence of unreacted carboxylic endgroups in the neutralized polymers needs a word of explanation. Polytetrafluoroethylene is an extremely inert, insoluble material, and carboxyl groups buried deep within a polymer particle are isolated from the attacking alkali. Unusually long periods of time were used in the titration in an effort to allow the alkali to diffuse into the polymer and react with these endgroups. This was not possible within reasonable lengths of time, so free carboxylic groups remained.

It has generally been assumed that termination of the polymer chains growing in an aqueous media occurs by combination, and arguments for

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TABLE II
 Infrared Absorption Spectra of the Various Tetrafluoroethylene Polymers

Expt.	Initiator, g.	Temp., °C.	Polymer, g.	\bar{M}_n^a	Infrared absorption spectra		
					Before titration	After titration	After pyrolysis
1	0.40	85	18	2,150,000	Bands at 2.81, 3.20, 5.52, and 5.62	Decrease in 5.62 and 5.52 Increase in 5.93	Bands only at 5.60 and 7.2
2	0.40	85-86	10	1,350,000	2.81, 3.20, 5.52, and 5.62	28% decrease in 2.81. 35% decrease in 3.20. Strong band at 5.93	Weak band at 5.62. Stronger band at 5.60
3	0.80	85	18	500,000	As above—strong	As above	No change (not heated enough)
4	0.80	90	12	350,000	As above—strong	40% decrease in 2.81. 55% decrease in 3.20. Medium band at 5.93	Medium band at 5.60

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this assumption are presented elsewhere.⁹ If an appreciable portion of the termination took place through a disproportionation reaction, the absorption at 5.60 typical of



terminal olefin should have been observed when the original sample was scanned in the infrared. Such was not the case. Termination by transfer reactions probably did not occur to any great extent, since the growing perfluoroalkyl chain is not reactive enough to abstract fluorine from the fluorocarbon polymer or monomer. Finally, since hydrogen-containing impurities were rigorously excluded from the polymerization recipe, little or no hydrogen-bearing ends would be expected. The oxidative hydrolysis of tetrafluoroethylene to difluoroacetic acid, a hydrogen-bearing entity, under the conditions of the polymerization, would not be significant.

The authors wish to acknowledge support and guidance provided by Dr. J. W. Haught during the course of this work, and the assistance of Drs. R. E. Moynihan and R. D. Nelson in the infrared work.

References

- (1) K. L. Berry and J. H. Peterson, *J. Am. Chem. Soc.*, **73**, 5195 (1951).
- (2) I. M. Koltoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951); P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **71**, 1419 (1949); J. Y. McDonald, *Trans. Faraday Soc.*, **42**, 193 (1946); and D. Bunn, *ibid.*, **42**, 190 (1946).
- (3) M. Hauptschein, C. S. Stokes, and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 1974 (1952); K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).
- (4) British Patent 719,574, *Improvements in or Related to New Fluorocarbon Acyl Sulfuric Acids*, John F. Dowd to Minnesota Mining and Manufacturing Company.
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- (6) J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **75**, 4525 (1953).
- (7) H. Simons, *Fluorine Chemistry*, Vol. II, Academic Press, 1954, Chap. 7.
- (8) M. Iwasaki, M. Aoki, and R. Kojima, *J. Polymer Sci.*, **25**, 377 (1957).
- (9) R. C. Doban, A. C. Knight, J. H. Peterson, and C. A. Sperati, Paper presented at the Meeting of the American Chemical Society, Atlantic City, September 1956.

Synopsis

The aqueous polymerization of tetrafluoroethylene initiated with ammonium persulfate in neutral or relatively weak acid solutions leads to polymer containing carboxyl end groups. The conversion of this endgroup to the sodium salt and its pyrolysis to the terminal olefin was followed, using infrared absorption technique.

Résumé

La polymérisation en milieu aqueux du tétrafluoroéthylène initiée avec du persulfate d'ammonium en solutions neutre ou peu acide fournit un polymère contenant des groupes carboxyles terminaux. La transformation de ce groupe terminal en sel sodé et sa pyrolyse en oléfine a été suivie par des techniques d'absorption infrarouge.

Zusammenfassung

Die Polymerisation von Tetrafluoräthylen in wässrigem Medium führt bei Anregung mit Ammoniumpersulfat in neutraler oder verhältnismässig schwach saurer Lösung zu Polymeren, die Karboxylendgruppen enthalten. Die Umwandlung dieser Endgruppe in das Natriumsalz und die Pyrolyse zum endständigen Olefin wurde durch Infrarotabsorptionsmessungen verfolgt.

Received July 22, 1958

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DuPont - FAP 9B3459

Method for determining total
fluorine and for determining
inorganic fluoride.

Total fluorine - fluoride =
organic fluorine

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MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Petitions Control Branch, HFF-334
Attn: J. Smith

DATE: November 9, 1978

FROM : C. J. Kokoski
Food Additives Evaluation Branch, HFF-185
Judy C. Edwards T.R. Carson 11/17/78
Judy C. Edwards/T.R. Carson
Division of Toxicology, HFF-185

SUBJECT: To amend 177.1520 and 175.300 to provide for use of Flourine
chemically treated or reacted with Polyethylene

FOOD ADDITIVE PETITION No. 8B-3394
Pre-File Review

Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, New York 10987

Petition is not suitable for filing. No toxicity data has been submitted.

What is the source of irradiation of the polyethylene polymer? Is the ionized radiation the same as provided for regulation 179.45 (121.2543)? If not, we will need the source and amount of radiation. Is the fluoride ion free or organic, such as ethylene fluoride of the low molecular weight fraction (LMWF)? If it is organic fluoride of LMWF, we have no toxicity data. Other toxicity data needed will depend upon the amount and nature of extractives.

No toxicity data is submitted with this proposal.

INIT:CJKokoski *CJK 11/20/78*

(b) (5)



000122

November 27, 1978

Mr. Reginald S. Pender
Union Carbide Corporation
Tarrytown Technical Center
Old Saw Mill River Road
Tarrytown, NY 10591

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Re: Food Additive Petition No. 8B3394

Dear Mr. Pender:

This will acknowledge receipt of your letter dated October 20, 1978 supplementing information contained in the above referenced food additive petition.

We have added this new material to our petition jackets and further action awaits scientific review.

Sincerely yours,

Brenda F. Finch
Petitions Control Branch, HFF-334
Division of Food & Color Additives
Bureau of Foods

(b) (5)



000123

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Petitions Control Branch, HFF-334
Attention: Julius Smith

DATE: JAN 17 1979

FROM : Chief, Environmental and Economic Impact Staff, HFF-407

SUBJECT: Environmental Review - FAP 8B 3394

I have reviewed the new EIAR and find that the petitioner is not responsive to your memorandum of July 20, 1978. Specifically, the petitioner has
1) not submitted the EIAR in the format specified in Section 25.1(j),
2) not utilized the guidance presented on pages 8-17 of the Operational Directive, and, 3) incorrectly cited old Section 21 CFR 6.1(c) regarding amendments to existing regulations.

However, because of the nature of the action I will probably be able to complete the assessment on receipt of the following:

1. information described in item A. 1-6 on page 10 of the Operational Directive;
2. information on the rate of introduction (if any), of the additive through manufacture, use and disposal (see Operational Directive, item B. page 11) and,
3. certification that the scrubber waste is being disposed of in compliance with all Federal, state and local standards (see 25.1(j)D.2.c.(3)).

The petitioner may use information presented elsewhere in the jacket and incorporate any of this information by reference in the EIAR. However, the petitioner should be informed that the EIAR is a public document which should essentially stand by itself.

If you have any questions, please advise.


Buzz L. Hoffmann, Ph.D.

(b) (5)



000124

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Petitions Control Branch, HFF-334
Attn: J. Smith

DATE: Feb. 8, 1979

FROM : Residue Analysis & Methods Investigation Branch, HFF-144

SUBJECT: FAP 8B3394 - Union Carbide Corp.
Submission Of 10-20-78.

The subject submission is only partially responsive to the questions raised in your letter of 7-20-78. The petitioner's responses will be evaluated in the order of the comments in your letter.

a. The petitioner has not provided additional information on the chemical nature of the modified surface layer or on how much fluorine actually becomes bonded to the polyethylene. Rather, he refers us to page 5 of the petition. The statements on this page concerning the chemical structure of the fluorinated surface layer are vague at best. The petition does mention weight gain measurements on films exposed to an
(b) (4)

there is no information in the petition on the percent fluorine incorporated into the treated polyethylene. ✓

b. The petitioner states that the sample of fluorinated polyethylene used for the IR spectrum had been treated with
(b) (4)

c. In response to your request for additional information regarding the manufacturing process, the petitioner has provided a copy of U.S. 3,998,180 assigned to Union Carbide. The patent describes the apparatus used for the fluorination as well as the range of treatment conditions (time and temperature, fluorine concentration) which could be used. The petitioner also states in the subject submission that normally both the internal and external surfaces of the polyethylene article would be treated.

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d. Regarding the concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation, the petitioner refers us to pages 3 and 5 of the petition.

(b) (4)

concentration." Rather than typical or usual conditions, we need to know what are the most severe treatment conditions anticipated. More specifically, are the following the maximum anticipated exposure conditions for the irradiated and non-irradiated polyethylene containers?

Irradiated*

Non-Irradiated*

(b) (4)

If not, then we need equilibrium extraction data using containers treated under the maximum exposure conditions which the proposed regulation is intended to cover. In the latest submission, the petitioner states that exposure

(b) (4)

This is just the reverse of the conditions given above. The petitioner should be required to clarify this point.

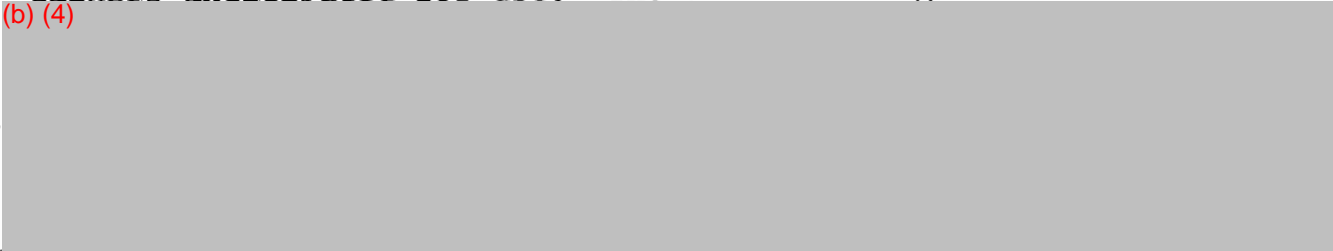
In response to the question concerning the inert diluent gases which will be used, the petitioner again refers us to page 3 of the petition.

Nitrogen gas is the only other ingredient in this process of surface modification and is used as an inert diluent for the fluorine gas.

However, on page 2 of the petition we find the phrase, "in an inert gas, such as nitrogen." The patent included with this submission discusses the use of inert diluent gases such as nitrogen or helium as well as reactive diluents like oxygen, sulfur dioxide, chlorine, bromine, nitrous oxide and certain unspecified organic monomers. Moreover, the revised proposed regulation included with this submission states that the polyethylene articles are surface modified "by the action of fluorine gas in combination with other gases such as nitrogen as inert diluents..." We again request the petitioner to clarify this point. Will other diluent gases besides nitrogen be used?

* See Table XV, p. 32 of the petition.

e. The petitioner states that it is difficult to determine the thickness of the fluorinated surface layer in the containers anticipated for use. The thickness ought to be less (b) (4)



f. The petitioner has provided a copy of the report from Schwarzkopf Microanalytical Laboratory regarding the analysis of the total extractives. The petitioner also states that the analysis was performed on the total non-volatiles from an extraction (with water as the food simulating solvent) conducted at 250°F for two hours. The analysis shows that virtually all of the fluorine in the water extract existed as F⁻ and not as organic fluoride bound to the polymer.

The petitioner should be required to explain the origin of the inorganic fluoride ion in the extractives. An IR spectrum of fluorinated high density polyethylene film furnished by the petitioner (Figure 1, p. 43 of the original petition) shows an absorption at about (b) (4) which is absent in the spectrum of the untreated film. This absorption is consistent with the formation of C-F covalent bonds in the modified surface layer as a result of the fluorination. Such bonds are not easily hydrolyzed. Inorganic fluoride ion is detected in the extracts when perfluorocarbon resins are extracted with food simulating solvents but this is apparently due to hydrolysis of the end groups introduced into the polymer through the use of persulfate initiators (Bro, M. I. and Sperati, C. A., J. Polym. Sci. 38, 289 (1959)).

g. The petitioner has submitted a revised proposed regulation. The question concerning the phrase "with other gases such as nitrogen as inert diluents," was already discussed above. In addition the proposed regulation does not mention fluorination of irradiated polyethylene containers (intended for aerosol applications). Regarding these irradiated containers, the petitioner should be required to state the type and source of the radiation to be used as well as the maximum dose which is anticipated. The petitioner should also clarify whether the containers are to be irradiated before or after fluorination (Tables VIII through XI give extraction data on irradiated first then fluorinated as well as fluorinated first, then irradiated containers).

Conclusions

The petition is not ready for filing. Since there are still a large number of unanswered questions, including some which the petitioner seems unwilling or unable to answer, we suggest that a meeting with Union Carbide might be useful at this time.

Patricia S. Schwartz

Patricia S. Schwartz, Ph.D.

(b) (5)

000128

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

TO : Ms. Brenda F. Finch
Petitions Control Branch, (HFF-334)

DATE: March 12, 1979

FROM : Dr. J. H. Khalsa *J. H. Khalsa*
Food Additives Evaluation Branch (HFF-185) *3/13/79*

SUBJECT: To amend 21 CFR, 177.1520 and 175.300 to provide for use of fluorine treated polyethylene (Olefin polymers) in producing, manufacturing, processing, treating, packaging, transporting, or holding foods.

FOOD ADDITIVE PETITION NO. 8B-3394

Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, New York 10987

IDENTITY:

The data provided by the petitioner show that the subject resin, the chemical structure of which was not shown, is a surface modified polyethylene that is produced by treating polyethylene with a mixture of fluorine and nitrogen gases. This modified polyethylene is proposed for manufacturing molded containers.

RELATED PETITIONS:

FAP 1B-0207 The oral LD₅₀ of perfluorocarbon resin, which is composed of mainly, polytetrafluoroethylene, in albino rats was 4g/kg. There were no toxic effects observed during a 7-day period of observation. The resin was approved on the basis of "virtually nil migration", which was 0.03 ppm (see the Toxicology memo by Dr. Misra, HFF-185, dated 4/16/75).

MIGRATION:

The extraction studies were performed on 8 oz. fluorinated polyethylene bottles, each of which had internal surface area of 37.99 sq. in. The irradiated polyethylene bottle that is intended for pressurized (aerosol)

(b) (4)

as summarized in Table I. The amount of fluoride ion (F⁻) in the extracts was determined by potentiometric fluoride ion analysis with the detection limit of 0.025 ppm of F⁻.

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Table I

(F⁻ Concentration in ppm)

<u>Food-simulating solvent</u>	<u>Temp./Time (in hrs)</u>	<u>Irradiated Container*</u>	<u>Non-irradiated Container</u>
Distilled water	250°F/2	2.30	1.03
50% ethanol/water	160°F/2	1.70	0.68
3% acetic acid/water	212°F/2	1.43	0.40
n-heptane	150°F/2	0.21**	0.041**

*Fluoridation, not irradiation.

**Values were not divided by 5.

Further, the analysis of total extractives made by an unnamed laboratory showed that all fluoride extracted from the polymer was inorganic F⁻ and no polymerically bound fluoride was detected. As pointed out in the Chemistry memorandum of 6/7/78, the migration values of fluoride should be evaluated in light of the allowable limits for fluoride ion in residential and industrial water supplies and inbottled water both at 1 ppm.

TOXICOLOGY:

The petitioner has not provided any toxicologic data to assess safety of fluorinated polyethylene.

CONCLUSION:

1. The food additive petition No. 8B-3394 is not suitable for filing at this time.
2. The Residue Analysis and Methods Investigations Branch (HFF-144) has sought additional information, and that could influence the chemical identification of what could become a food additive.
3. No toxicity data is provided by the petitioner. This division will require a safety rationale for the proposed use.

(b) (5)

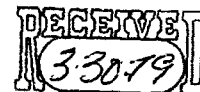


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Judy CJK
COPY IN FILE

March 28, 1979



Mr. Reginald S. Fender
Union Carbide Corporation
Tarrytown Technical Center
Route 1000
Saw Mill River Road
Tarrytown, NY 10591

BEST ORIGINAL COPY

Re: FAP No. 8E3394

Dear Mr. Fender:

This is in response to your correspondence dated September 14, 1978, submitted under the cover letter of October 20, 1978, relative to the food additive petition referenced above.

The subject submission is only partially responsive to the questions raised in our letter of 7-20-78. You have satisfactorily responded to questions (b), (c) and (e) of our letter, however, the following are our comments concerning (a), (d), (f), (g) and (h).

Question (a):

Additional information on the chemical nature of the modified surface layer or on how much fluorine actually becomes bonded to the polyethylene has not been provided. Rather, you refer us to page 5 of the petition. The statements on this page concerning the chemical structure of the fluorinated surface layer are vague at best. The petition does mention weight gain measurements on films exposed to an

(b) (4)

(b) (4)

however, there is no information in the petition on the percent fluorine incorporated into the treated polyethylene.

Question (d):

Regarding the concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation, you refer us to pages 3 and

(b) (4)

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less period of exposure as the "usual duration for this gas concentration." Rather than typical or usual conditions, we need to know what are the most severe treatment conditions anticipated. More specifically, are the following the maximum anticipated exposure conditions for the irradiated and non-irradiated polyethylene containers?

Irradiated*
(b) (4)

Non-Irradiated*

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*Table XV, p 32 of the petition

If not, then we need equilibrium extraction data using containers treated under the maximum exposure conditions which the proposed regulation is intended to cover. In the latest submission, you state that exposure temperatures are approximately 180°F for the higher fluorine concentration and 110°F for the lower (b) (4) fluorine concentration. This is just the reverse of the conditions given above. You should clarify this point.

In response to the question concerning the inert diluent gases which will be used, you again refer us to page 3 of the petition.

Nitrogen gas is the only other ingredient in this process of surface modification and is used as an inert diluent for the fluorine gas.

However, on page 2 of the petition we find the phrase, "in an inert gas, such as nitrogen." The patent included with your submission discusses the use of inert diluent gases such as nitrogen or helium as well as reactive diluents like oxygen, sulfur dioxide, chlorine, bromine, nitrous oxide and certain unspecified organic monomers. Moreover, the revised proposed regulation included with this submission states that the polyethylene articles are surface modified "by the action of fluorine gas in combination with other gases such as nitrogen as inert diluents...." You should also clarify this point. Will other diluent gases besides nitrogen be used? If so, what other gases will be used?

Question (f):

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You provided a copy of the report from Schwarzkopf Microanalytical Laboratory regarding the analysis of the total extractives. You also state that the analysis was performed on the total non-volatiles from

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an extraction (with water as the food simulating solvent) conducted at 250°F for two hours. The analysis shows that virtually all of the fluorine in the water extract existed as F⁻ and not as organic fluoride bound to the polymer.

You should explain the origin of the inorganic fluoride ion in the extractives. Your explanation should also address the fact that an IR spectrum of fluorinated high density polyethylene film furnished (Figure 1, p. 43 of the original petition) shows an absorption at (b) (4) which is absent in the spectrum of the untreated film. This absorption is consistent with the formation of C-F covalent bonds in the modified surface layer as a result of the fluorination. Such bonds are not easily hydrolyzed.

Question (g):

You have submitted a revised proposed regulation. The question concerning the phrase "with other gases such as nitrogen as inert diluents" was already discussed above. In addition the proposed regulation does not mention fluorination of irradiated polyethylene containers (intended for aerosol applications). Regarding these irradiated containers, you should indicate the type and source of the radiation to be used as well as the maximum dose which is anticipated. You should also clarify whether the containers are to be irradiated before or after fluorination (Tables VIII through XI give extraction data on irradiated first then fluorinated, as well as fluorinated first then irradiated containers).

Question (h):

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We have reviewed the new EIAF and find that it is not responsive to our letter of July 20, 1978. Specifically, you have 1) not submitted the EIAF in the format specified in Section 25.1(j), 2) not utilized the guidance presented on pages 8-17 of the Operational Directive, and, 3) incorrectly cited old Section 21 CFR 1.1(c) regarding amendments to existing regulations.

We will be able to complete the assessment on receipt of the following:

1. An EIAF in the format specified in §25.1(j) (copy enclosed);
2. Information described in item A. 1-6 on page 10 of the Operational Directive (copy enclosed);

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Page 4 - Mr. Reginald S. Pender

3. Information on the rate of introduction (if any), of the additive through manufacture, use, and disposal (see Operational Directive, item I. page 11) and;
4. certification that the scrubber waste is being disposed of in compliance with all Federal, state and local standards (see 25.1(j)L.2.c.(3)).

In collecting the data requested above, you may use information presented elsewhere in the petition and incorporate any of this information in the EIAR. However, in the preparation of the EIAR, you should keep in mind that the EIAR is a public document which should essentially stand by itself.

Our toxicological review of the petition indicates that no toxicity data was submitted. However, our final comment's relative to required toxicity data will depend upon the amount and nature of the extractives.

In conclusion, the petition is unacceptable for filing. Since there are still a large number of unanswered questions, we suggest that a meeting with you might be useful.

Sincerely yours,

Julius Smith.
Petition Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods

(b) (5)



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January 27, 1981

Mr. Reginald S. Pender
Union Carbide Corporation
Tarrytown Technical Center
Route 100 C
Saw Mill River Road
Tarrytown, NY 10591

Re: FAP No. 883394

Dear Mr. Pender:

This is in further regard to our letter of March 28, 1979 concerning the above referenced petition to provide for the safe use of fluorinated polyethylene in producing, manufacturing, processing, preparing, packaging, transporting or holding food.

To date we have not received a response to the March 28, 1979 letter. If no data are received within 30 days of the date of this letter, the referenced food additives petition will be dropped from review and retired to our archives. It would then be necessary to submit a new food additive petition if you want further consideration of this material.

Sincerely yours,

Julius Smith
Petitions Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods

(b) (5)

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000135

February 5, 1981

Mr. Reginald S. Pender
Union Carbide Corporation
Tarrytown Technical Center
Route 100 C
Saw Mill River Road
Tarrytown, NY 10591

Re: FAP No. 8B3394

Dear Mr. Pender:

As stated during our telephone conversation of Thursday afternoon,
February 5, 1981, enclosed is a copy of the March 28, 1979 letter which
you requested.

Sincerely yours,

Julius Smith
Petitions Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods

(b) (5)



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000136

914- 789-2207



UNION CARBIDE CORPORATION
SILICONES & URETHANE INTERMEDIATES DIVISION
OLD SAW MILL RIVER ROAD, TARRYTOWN, NEW YORK 10591

RESEARCH AND DEVELOPMENT

February 12, 1981

Mr. Julius Smith
Department of Health and Human Services
Public Health Service
Food and Drug Administration
Petition Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods
200 C Street, S. W.
Washington, D.C. 20204

Re: FAP No. 8B3394

BEST ORIGINAL COPY

Dear Mr. Smith:

In response to your letter of January 27, 1981 and our telephone conversation of February 5, 1981, Union Carbide Corporation respectfully requests that the above referenced petition regarding, "the safe use of fluorinated polyethylene in producing manufacturing, processing, preparing, packaging, transporting, or holding food" remain active.

It is fully our intention to make the appropriate responses to your previous letter at the earliest time possible. We request further, however, that you waive the thirty-day deadline from the January 27, 1981 date to an extended period to allow me, as the Corporation's agent, to reconvene my files on this matter and to consolidate the necessary information to adequately reply to your remaining questions and comments.

Appreciatively,

A handwritten signature in dark ink, appearing to read "R. S. Pender", written over a large, stylized circular flourish.

R. S. Pender

(b) (5)

A solid black rectangular redaction box covering several lines of text in the bottom left corner of the page.

000137

February 18, 1982

Mr. Reginald S. Pender
Union Carbide Corporation
Tarrytown Technical Center
Route 100 C
Saw Mill River Road
Tarrytown, NY 10591

Re: FAP No. 8B3394

Dear Mr. Pender:

This is in further regard to our letters of March 28, 1979 and January 27, 1981 concerning the above referenced petition to provide for the safe use of fluorinated polyethylene in producing, manufacturing, processing, preparing, packaging, transporting or holding food.

In response to our letter of January 27, 1981, you requested in your letter February 12, 1981 that the above referenced food additive petition remain in our active file. You also stated that the requested data would be forthcoming.

However, to date we have not received a substantive response to the March 28, 1979 letter. If no data are received within 30 days of the date of this letter, the referenced food additives petition will be dropped from review and retired to our archives. It would then be necessary to submit a new food additive petition if you want further consideration of this material.

Sincerely yours,

Julius Smith
Petitions Control Branch, HFF-334
Division of Food & Color Additives
Bureau of Foods

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(b) (5)



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Union Carbide Corporation
National Specialty Gas Office
P.O. Box 444 100 Davidson Ave.
Somerset, New Jersey 08873

March 31, 1982

FAP 3394

Mr. Julius Smith
Petitions Control Branch
HFF 334
Food & Drug Administration
200 C Street S.W.
Washington, D.C. 20204

Subject: FDA Approval of Surface Modified Plastic Containers
Reference: Our telephone conversation of March 30, 1982

Dear Mr. Smith:

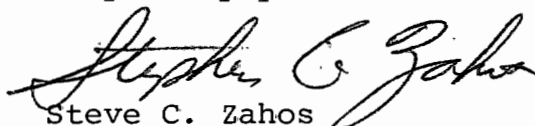
Many thanks for your call yesterday to follow up on the subject approval. Much has happened since Union Carbide last actively pursued this approval; mainly, the technology was passed from a Corporate Research & Development Group to the Linde Division. Your recent correspondence to our Mr. Pender was routed to the wrong individual.

Nevertheless, please be assured that Union Carbide wishes to keep its petition file open. I have been assigned to coordinate the effort between this group, FDA and our divisional FDA interface. In the future you may direct correspondence to my attention.

As soon as we receive your recent letter to Mr. Pender from him, we will do all we can to assemble and to send the required data to you in a timely fashion. When it is ready I will call to discuss the best way to present the information to you, in person or by written letter. Until then, thank you again for your call.

Looking forward to dealing with you again soon.

Very truly yours,


Steve C. Zahos
Marketing Specialist
Surface Modified Plastics

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(b) (5)



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UNION CARBIDE CORPORATION

OLD SAW MILL RIVER ROAD, TARRYTOWN, NY 10591

Research and Development

Silicones & Urethane Intermediates Division

August 23, 1982

Mr. Julius Smith
Petitions Control Branch, HFF-334
Division of Food & Color Additives
Bureau of Foods,
Food & Drug Administrations
Department of Health & Human Services
Washington, DC. 20204

RE: FAP No. 8B3394

Dear Mr. Smith:

I extend my apologies for the long delay and my gratitude for your indulgence in awaiting this response to your letter of 28 March, 1979. As you are probably aware, through our written correspondence and telephone conversations, this long interim was due to my having been assigned different responsibilities at a different Union Carbide location and the project's responsibility being transferred between corporate divisions and to different personnel.

It was recently decided that I should, finally, re-acquire the responsibility for completing the requirements for the cited food additive petition.

The responses to your questions and comments contained in the aforementioned letter are contained herewith. It is hoped that these responses clear up any misunderstandings or shortcomings of the original petition and satisfy the requirements for a new regulation allowing pursuit of Union Carbide's process for manufacturing fluorated polyethylene for food and/or drug contact use applications.

If you have any further need to contact me, please do not hesitate to telephone my office at (914)789-2207 or write to me here at Union Carbide in Tarrytown.

Sincerely yours,

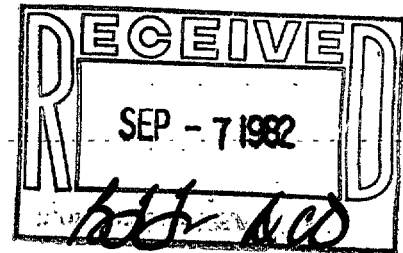
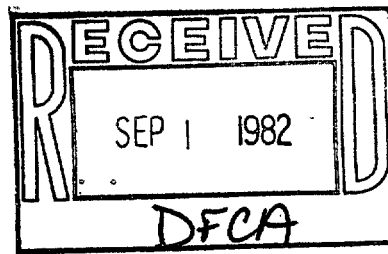
R.S. Pender

(b) (5)

attach.

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UNION CARBIDE CORPORATION

OLD SAW MILL RIVER ROAD, TARRYTOWN, NY 10591

Research and Development

Silicones & Urethane Intermediates Division

August 24, 1982

Mr. Julius Smith
Petition Control Branch, HFF-334
Division of Food & Color Additives
Bureau of Foods
Food & Drug Administration
Dept. of Health and Human Services
Washington, D.C. 20204

RE: FAP 8B 3394

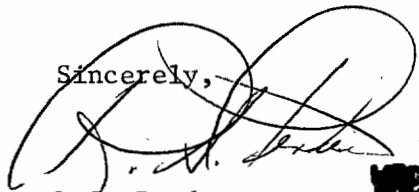
Dear Mr. Smith:

As a follow-up to our telephone conversation of 19 August, this letter will serve as Union Carbide's formal request for a continuance of consideration for the above cited Food Additive Petition beyond the currently set expiration date of September 6, 1982.

The informational responses requested by your offices have been drafted and are currently in preparation for submission to you and should arrive sufficiently in advance of that 6 Sept. deadline.

During the interim, however, in the event delivery of that documentation is delayed, we would appreciate any consideration given to a time extension as per this request.

Sincerely,

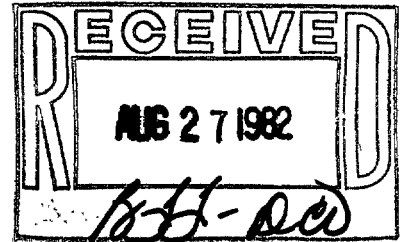
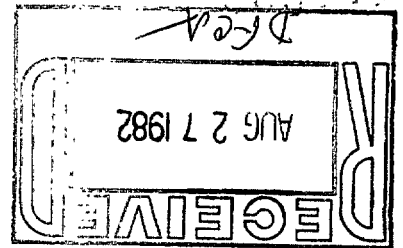

R.S. Pender

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(b) (5)

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Page 1
Mr. Julius Smith

August 25, 1982
Re: FAP-8B3394

Question (a)

Additional information on the chemical nature of the modified surface layer or on how much fluorine actually becomes bonded to the polyethylene has not been provided. Rather, you refer us to page 5 of the petition. The statements on this page concerning the chemical structure of the fluorinated surface layer are vague at best. The petition does mention weight gain measurements on

(b) (4)

(b) (4)

However, there is no information in the petition on the percent fluorine incorporated into the treated polyethylene.

Point (a) Response

(b) (4)

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Question (c)

Regarding the concentration of fluorine in the gas mixture and the time/temperature conditions of treatment for each type of container to be covered in the proposed regulation, you refer us to pages 3 and 5 of the petition.

(b) (4)

tion for this gas concentration." Rather than typical or usual conditions, we need to know what are the most severe treatment conditions anticipated. More specifically, are the following the maximum anticipated exposure conditions for the irradiated and non-irradiated polyethylene containers?

Irradiated*

Non-Irradiated*

(b) (4)

*Table XV, p 32 of the petition.

If not, then we need equilibrium extraction data using containers treated under the maximum exposure conditions which the proposed regulation is

(b) (4)

of the conditions given above. You should clarify this point.

In response to the question concerning the inert deluent gases which will be used, you again refer us to page 3 of the petition.

Nitrogen gas is the only other ingredient in this process of surface modification and is used as an inert diluent for the fluorine gas.

However, on page 2 of the petition we find the phrase, "in an inert gas, such as nitrogen." The patent included with your submission discusses the use of inert diluent gases such as nitrogen or helium as well as reactive diluents like oxygen, sulfur dioxide, chlorine, bromine, nitrous oxide, and certain unspecified organic monomers. Moreover, the revised proposed regulation included with this submission states that the polyethylene articles are surface modified "by the action of fluorine gas in combination with other gases such as nitrogen as inert diluents...." You should also clarify this point. Will other diluent gases besides nitrogen be used? If so, what other gases will be used?

Point (c) Response

Responding again to the point of inert diluents first, nitrogen (N₂) gas is the only inert diluent anticipated and proposed for use in this fluorine treatment where such end product material would have use in food and/or drug contact applications. From the considerations of economics, availability, and

convenience, nitrogen gas is the only choice of current practicality and ideally suited to our needs in this application. Use of the phrase "such as" preceding the word "nitrogen," is perhaps confusing but was simply a phraseological allusion to its reference in the U.S. patent number 3,998,180. Such patent coverage is an umbrella, inclusive of all our fluorination processes afforded by the uniqueness of Union Carbide's designed equipment and procedures. The other gases referenced in the patent and cited in your letter do have application in combination with fluorine in areas outside food and drug or other human consumption situations.

The treatment gas concentrations as referenced in your letter do, in fact, represent the maximum F_2 gas concentrations anticipated for use in applications where food and/or drug contact end use is involved.

Through a heretofore undetected typographical error, the time and temperature references of irradiated and non-irradiated polyethylene bottles are in fact reversed in Table XV as you cited. The correct concentrations and time and temperature conditions should read as follows:

<u>Irradiated</u>	<u>Non-Irradiated</u>
(b) (4)	

The above is the order given in the most previous submission that you also cite in your letter.

In any case of anticipated use for food and/or drug applications, the most

(b) (4)

Question (f)

You provided a copy of the report from Schwarzkopf Microanalytical Laboratory regarding the analysis of the total extractives. You also state that the analysis was performed on the total non-volatiles from an extraction (with water as the food simulating solvent) conducted at 250°F for two hours. The analysis shows that virtually all of the fluorine in the water extract existed as F⁻ and not as organic fluoride bound to the polymer.

You should explain the origin of the inorganic fluoride ion in the extractives. Your explanation should also address the fact that an IR spectrum of fluorinated high density polyethylene film furnished (Figure 1 on 12 of the original petition) shows an absorption at about (b) (4) the spectrum of the untreated film. This absorption is consistent with the formation of C-F covalent bonds in the modified surface layer as a result of the fluorination. Such bonds are not easily hydrolyzed.

Point (f) Response

As noted in your question, the referenced analysis does list all detectable fluoride from an extraction with water at 250°F for 2 hours as ionically existent and not polymerically bound organic fluoride. It is also correct that the infrared absorption band at [redacted] is consistent with and is in fact a carbon fluorine bond and is not hydrolyzed in aqueous sterilization of the treated polyethylene.

The ionic fluoride (F⁻) detected analytically derives from, we believe, two avenues.

(b) (4)



Page 5
Mr. Julius Smith

August 25, 1982
Re: FAP-8B3394

(b) (4)



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Question (g)

You have submitted a revised proposed regulation. The question concerning the phrase "with other gases such as nitrogen as inert diluents" was already discussed above. In addition the proposed regulation does not mention fluorination of irradiated polyethylene containers (intended for aerosol applications). Regarding these irradiated containers, you should indicate the type and source of this radiation to be used as well as the maximum dose which is anticipated. You should also clarify whether the containers are to be irradiated before or after fluorination (Tables VIII through XI give extraction data on irradiated first then fluorinated, as well as fluorinated first then irradiated containers).

Point (g) Response

Such change to correct the proposed regulation has been made with the elimination of the word "..other gasses such as" amending that referenced line of the proposal to read: "..with gaseous nitrogen as an inert diluent."

Such amended regulation is included herewith as the immediately successive two (2) pages.

Regarding the question on container irradiation, Union Carbide does not seek, at this time, to have included in the regulation for fluorinated polyethylene as food contact items, a provision for an irradiation step.

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INDIRECT FOOD ADDITIVE PETITION NO. 8B3394

PROPOSED REGULATION

Title 21 - FOOD and DRUGS

CHAPTER 1- FOOD and DRUG ADMINISTRATION

Department of Health, Education, and Welfare

Subchapter B- Food and Food Products

Part 177 - Indirect Food Additives; POLYMERS

Subpart B - Substances for use as basic components of single and repeated use food contact surfaces.

FLUORINATED POLYETHYLENE

The Commissioner of Food and Drugs, having evaluated the data in a petition (8B3394) filed by Union Carbide Corporation, Old Ridgebury Road, Danbury, Connecticut 06817 and other relevant material, concludes that the food additive regulations should be amended as set forth below, to provide for the safe use of fluorinated polyethylene as articles intended for use in contact with foods.

Therefore, pursuant to the provisions of the Federal Food, Drug, and Cosmetic Act (sec 409 (c), 72 Stat. 1786; 21 U.S.C. 348 (c) (1) and under authority delegated to the Commissioner, (21 CFR 177) is amended by inserting in the list of substances a new regulation as follows:

Polyethylene, Fluorinated

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food contact articles in accordance with the following prescribed conditions:

(a) Fluorinated Polyethylene food contact articles are produced when polyethylene articles are surface modified by action of fluorine gas in combination with gaseous nitrogen as an inert diluent with such action leaving the polymer's bulk unchanged. Fluorine gas shall be used in concentrations not in excess of amounts necessary to achieve the intended technical effect in the food or drug contact article.

(b) Polyethylene articles shall be fluorinated from basic resins identified and defined in 177.1520 paragraph (a) (2) and paragraph (a) (3) and shall conform to the specifications of paragraph (c) (2-1) and paragraph (c) (3-1).

August 25, 1982
Re: FAP-8B3394

(c) The finished food contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of 176.170 (c) of this chapter, yields fluoride ion not to exceed 5 ppm calculated on the basis of the volume held by the food contact article when tested by the methods described in 177.1330 (c).

(Note; in testing the finished food contact article, use a separate test sample for each extracting solvent.)

Page 9
Mr. Julius Smith

August 25, 1982
Re: FAP-8B3394

Question (h)

We have reviewed the new EIAR and find that it is not responsive to our letter of July 20, 1978. Specifically, you have 1) not submitted the EIAR in the format specified in Section 25.1 (j); 2) not utilized the guidance presented on pages 8-17 of the Operational Directive; and 3) incorrectly cited old Section 21 CFR 6.1 (c) regarding amendments to existing regulations.

Point (h) Response

Such revised Environmental Impact Analysis Report has been made according to the Environmental Impact Operational Directive and pursuant to CFR 25.1 (j) and is herewith attached.

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Page 10
Mr. Julius Smith

August 25, 1982
Re: FAP-8B3394

ENVIRONMENTAL IMPACT ANALYSIS REPORT

Date: 13 August, 1982

Re: FAP No. 8B3394

Name of Applicant:
Union Carbide Corporation

Address of Applicant:

Old Ridgebury Road
Danbury, CT 06817

by: R. S. Pender

000151

A. Describe the Proposed Action

1- Completely Describe the Proposed Action

Union Carbide Corporation proposes that the Food and Drug Administration of the Health and Human Services Department amend 21 CFR 177 to include and allow the safe and pollution free manufacture of fluorinated polyethylene for acceptable use as food and/or drug contact articles where such articles have been prepared in a process involving formed polyethylene (film, bottles, etc.) being exposed to fluorine (F₂) gas in concentration to twenty-five (25) volume percent, in combination with nitrogen (N₂) gas as an inert diluent.

Further, we propose that in such manufacturing process, all reaction gas diluent gas and gaseous by-products of the process be handled and transferred at reduced pressure in a closed system of such design that the fluorine gas mix can be transferred repeatedly between a holding chamber and reaction (polyethylene exposure) chamber until depleted. In addition, such process shall be required to have provision for transferral of all depleted gases and gaseous by-products directly to a scrubber section of the closed system such that those gases are transformed to a safe, easily handled condition, as a metal fluoride in aqueous solution.

Further, this action proposes that the objects of this process (treated polyethylene) be removed from the reaction process chamber by remote, automatic means and only after such chamber and articles have been evacuated and purged of all reactive gases and by-products such that there is no operator or other human exposure conditions to the reaction treatment gases or by-products therefrom.

2- Describe the Chemical and Physical Properties of the Product

The object of our proposed process acceptance is the creation of unique surface alteration on the long accepted and GRAS polyethylene with that material's interior bulk unchanged. Thus, Union Carbide's surface modified polyethylene retains many of the inherent properties of its material of derivation. The radical departure in properties of such surface altered polyethylene lies in its reduced permeability by certain gases, such as carbon dioxide and oxygen, and resistance to certain solvents such as hexane and xylene, and overall improved physical integrity.

Due to the nature of our process, this modified surface exists as an integrally bound layer of up to only (b) (4) thickness, but with significantly decreased porosity, from that of polyethylene, due in part to process generated surface crosslinks.

The resulting surface is essentially of the structure $(CH_2-CH_2)_n - (CH_2-CHF)_n' - (CH_2-CF_2)_n''$. This functional grouping is extensively distributed throughout the surface and is non-solubilized in any of the food simulating solvents (distilled water, 50% ethanol in water, heptane, and 3% acetic acid in water) according to test procedures as directed in FDA Guidelines for Chemistry and Technology Requirements of Indirect food Additive Petitions. Hence, these so treated container surface functionalities do not become direct or indirect food additives according to these FDA tests procedures nor according to some, we feel, more severe Union Carbide performed testing as detailed in FAP No. 8B3394.

3- Describe the Pharmacological/Toxicological Properties of the Product

As cited in FAP 8B3394, we believe that our proposed product manufacture and usage presents no public health hazards beyond those of ordinary polyethylene or other fluorine containing polymers that are currently GRAS and are in daily and widespread usage as food contact materials. We believe this based on the following:

When testing according to CFR 121-2501, which deals with acceptable levels of extractable residue from polymeric materials as they might become additives to food, our fluorine treatment generally resulted in reductions in the amount of total extractables from that of control, untreated, samples of identical resin. This was true in the cases with both solvents, hexane, and xylene, as called for and under conditions required in this regulation.

In all cases our treated specimens, as did our controls, fell well within the limits established for acceptable residue extractant as given by the procedure. Further under this cited testing, though residue identification is not a procedural requirement, infrared analyses of the xylene extracts reveal the same material spectra for both fluorinated and non-fluorinated polymer, ie.; no IR detectable fluorine bound species is removed as a xylene soluble.

When tested further for extractable fluoride according to CFR 121-2555 (a regulation for perfluorocarbons), we again and repeatedly come within the "safe" limits for ionic fluoride (See FAP 8B3394, p. 10 and Table XIV).

Further, when all of our test data for food contact materials according to FDA Guidelines for Chemistry and Technology of Indirect Food Additive Petitions and for container processes for which this petition is intended are compared to all federally allowed fluoride concentrations including Threshold Limit Value, Home and Industrial Water Fluoridation levels, Potable Water Level CFR 121-2555 Extractable level from Perfluorocarbons (eg. Teflon®), and the OSHA Airborne Tolerance level, extractable fluorides from Union Carbide processed products, under conditions of proposed use, are well within the accepted limits.

In addition, the commonly accepted, purchased, and used fluoridated toothpaste has an ionic fluoride incorporation level of 1000 ppm which exceeds the maximum extractable fluorides from the action of food simulating solvents on our fluorinated polyethylene by over four hundred (400) times.

With toothpaste being a commodity item of near universal domestic use several times daily per individual over the course of individual lifetimes, our maximum level of 2.3 ppm available extractant fluoride ion appears insignificant.

We believe it reasonable to assume that the degree of commercial acceptance or need for our proposed single use fluorinated container will not approach the universality of fluoridated toothpaste. Furthermore, we do not believe that the total fluoride consumed as a result of our container process will approach the relative level acquired through domestic water programs.

Even if we were to assume a 100% market penetration level and all food consumed by humans were from Union Carbide process fluorinated polyethylene containers, and we were, in addition, to take our case of highest extractable fluorides, (that of aqueous-container sterilized foods) and assumed further that the average 1500 gm/day diet were totally aqueous, then the maximum daily consumption of fluoride resultant as an indirect food additive would be approximately 31 ppm/day or 0.046 gm/day. If we were, however, to divide the average daily diet into its standard proportions of 133 gm fatty food and 455.67 gm each of aqueous acidic and alcoholic components, and assuming again exclusive use of our containers for a 1500 gm/day diet, then the maximum consumable fluoride declines to 7.5 ppm or 0.011 gm/day.

These figures are based on the maximum extractable fluoride by each of the appropriate food simulating solvents used in our studies according to FDA indirect food additive guidelines and detailed in FAP 8B3384.

Summarizing, even at the theoretical 100% market penetration level, our worst case figures for available consumable fluoride is relatively small, especially when compared to the non-theoretical but actual 1000 ppm fluoride content of toothpaste which is of well established consumer usage.

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4- Discuss the Anticipated Purposes and Benefits of the Proposed Action

The thrust of this proposed process is to increase the utility of relatively inexpensive and widely used polyethylene. The Union Carbide process of surface modification with fluorine effects this accomplishment without major increase in cost of finished articles formed of this polymer and without burden on the environment beyond that of ordinary polyethylene.

Polyethylene, as it is manufactured for use, has certain inherent limitations for food and drug containers applications. Among these limitations are its large permeability values to materials such as fluorocarbon fluids, hydrocarbon fluid (both aromatic and non aromatic), fats, oils, oxygen, and carbon dioxide. These and other limitations prohibit this relatively inexpensive polymer from use in many markets where its contents would be food and/or drugs and where, from a cost basis, it would otherwise be desirable.

Currently, application areas where those above stated or similar items are among the contents, are generally obliged to be satisfied by more expensive resins (eg. polyethylene terephthalate); less aesthetically pleasing containers (eg. metal cans), or less safe (breakable) material (eg. glass). This is despite the fact that polyethylene is an accepted FDA GRAS material.

Union Carbide's fluorination process largely overcomes these limitations by the creation of an integrally bound, thin surface layer that serves as an effective permeation and solvent resistant barrier.

Data obtained from tests comparing permeation rates of various organic permeant type solvents as contents of non-fluorinated and fluorinated polyethylene along with comparisons to more expensive, competitive materials, show that the polymer improvement by our fluorination process is substantial. Further, these data show that after treatment permeation levels are reduced to levels that rival those of the more expensive resins. In addition, extractant studies with food simulating solvents, as earlier discussed, make it apparent that major property enhancement is afforded to polyethylene by our process of modification.

These and additional data substantiating the aforementioned property improvements to polyethylene are completely documented as the section referenced "Tables" included with FAP 8B3394.

- 5- Estimate the Potential Market Penetration, Handling, Storage, and Distribution Schemes for a Particular Product

-and-

- 6- Describe Briefly the Primary Environments Affected by the Manufacture, Distribution, Consumption, and Disposal of the Product Subject to the Proposed Action.

As referenced in the discussion of A.4., where a market penetration level of 100% is assumed and extractive fluoride levels are given accordingly, primary environmentally affective components resultant of our process are in small concentration.

It is obvious, however, that markets of interest do not include all normal food applications.

A contention on our part that (b) (4) market share of all packaged consumer food items would be packaged in Union Carbide's process fluorinated polyethylene appears reasonable, but simultaneously optimistic.

If we were however to gain that 10% level of market penetration, potentially consumable fluoride would be on the order of 3.1 ppm per individual per day (approximately 0.005 gm F₂/day) for the totally aqueous diet and 0.75 ppm (0.001 gm/day for the average diversified diet, amounts which when compared to other sources of ingestible fluoride availability are insignificant. Since other extratives from our fluorinated polyethylene are essentially fragmented polyethylene, as is normal with this polymer, since no known gaseous products are evolved from containers so processed, and, since essentially all removable fluoride is extracted in the sterilization step, no extraordinary measures for handling, storage, distribution, and disposal of this product are required; that is, all normal routes for these individual and collective actions that are currently available to ordinary polyethylene and other commonly used polymeric materials should be equally available to fluorinated polyethylene.

The markets of interest for our single use container product are those currently served by other container materials. Thus, our entry to those markets would simply displace those other materials to the same extent as our penetration, yielding no anticipated net increase in the total number of containers generated. Our entry to these markets may produce a net increase in safety since certain applications now are only satisfactorily served by breakable and often injurious glass.

B. Discuss the Environmental Impact of the Proposed Action

1- Introduction into the Environment

As discussed previously in FAP 8B3384 and extensively in U.S. Patent 3,998,180, our process of surface modification is designed with provision for safe, efficient, and pollution free exposure of formed polyethylene articles to nitrogen (N_2) diluted fluorine (F_2) gas to render those articles less permeable and thus enhance their overall utility. The system accomplishing this is designed as a closed loop where the reactive gases are transferred back and forth repeatedly, in successive treatments of polyethylene exposure, between a holding tank and reaction chamber.

The gaseous transferral is accomplished by vacuum and in the process, reaction by-products are removed by passage of the gases through traps specific for HF and having no effect on the reactant gas mix.

This back and forth transferral continues until all the reactant gas mix is essentially depleted, whereupon the entire system's internal atmosphere is purged into a caustic scrubber. The remaining by-product HF and any trace F_2 gas is made safe and easy to handle by conversion to a metallic salt in aqueous solution. This solution can then be removed and disposed of in a manner compliant with all Federal, State, and local codes.

The process itself is designed such that it is carried out at relatively low temperature and at slightly reduced pressure in atmospherically sealed chambers. If any leakage should occur, it would be air leaking into the containment vessel rather than reactants leaking out to the human environment. If such should occur, air entry into the chamber would give ready notice; it would be observed both mechanically and electronically via vacuum/pressure monitoring devices detecting the approach toward equalization of the internal and external atmosphere pressures. At such observation point, solenoid controlled valves would then be operated to empty the reactor gaseous contents either back to the holding tank or directly to the scrubber.

It should be noted that any and all such process facilities operating according to this Union Carbide technology have as part of their design provision for auxilliary, emergency electrical generation to preclude the situation where a main power interruption might shut down electrically powered safety devices.

Hence, the potential for the buildup of internal pressure in the chamber and the possibility of leakage of fluorine gas to the atmosphere is made so remote as to be essentially eliminated.

Further, the reaction system is equipped so as to allow for the safe purging of the chamber with air or nitrogen gas or a combination thereof prior to access of operating personnel to the reactor's interior. The purge gas is also passed to the scrubber such that any deleterious product can be removed without mingling with the human environment.

2- Analysis of the Environmental Impact of the Manufacturing Process

Much of such analysis is presented and discussed in the immediately preceding sub-part 1 of this section.

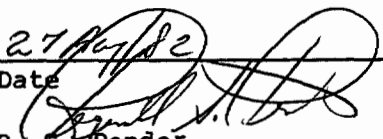
The environmental impact of the process overall is believed to be insignificant. This belief is advanced for a number of reasons among which is the fact that no known (detectable) emissions are yielded to the external atmosphere during the the introduction of reactive gas to the treatment chamber, during the reaction process, nor during the gaseous transfer from the chamber of treatment. In addition, the HF line traps employed in removal of consequential by-products are periodically removed from the system lines for regeneration with the products of such regeneration (waste) being driven to a scrubber. The scrubber as discussed earlier is also monitored, and when nearing depletion, the solution is safely pumped to containment vessels and disposed of in a manner compliant with all appropriate ordinances (Appendix A).

Resource use for this process involves the synthetic organic chemicals derived from petroleum feedstocks used in the current ordinary production of polyethylene along with elemental fluorine. Should the proposed action be implemented, raw materials and energy presently used to produce current, less technically and economically acceptable products would be diverted to production of the proposed product.

In summary, Union Carbide Corporation neither knows of nor foresees any adverse effect to the environment as a result of our proposed action of manufacturing fluorinated polyethylene as food contact articles.

Polyolefins such as polyethylene, which is the base material for this process, have been used many years as food contact articles and containers.

Fluorine containing materials including those with larger or similar extractable fluoride such as toothpaste, Teflon®, and potable water have also seen such usage and are generally recognized as safe (GRAS). In that light, Union Carbide as a responsible corporation expects or knows of no material or technical objection to this action.

27 Aug 82
Date 
R. S. Pender
for Union Carbide Corporation

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Appendix A

The waste products of the described process are managed in compliance with Code of Federal Regulations, Title 40, Parts 262, 263, 264, and 265, New Jersey Administrative Codes, Title 7, Chapters 26 and 27, and all applicable local ordinances.

The containment vessels of this waste product, D.O.T. Specification 5 steel drums with closed head and welded seams, are presently being stored in order to evaluate an on-site neutralization and detoxification process and for equipment development. This neutralization process involves the use of sulfuric acid to render the pH of the waste solution between 6.0 and 9.0. Within these limits, this material is not listed or characterized as a hazardous material under the Resource Conservation and Recovery Act (RCRA), nor is it identified as a hazardous substance under the Federal Water Pollution Control Act (FWPCA). The detoxification process involves the addition of calcium carbonate to the potassium fluoride waste solution to produce an insoluble, nontoxic salt, calcium fluoride which in its naturally occurring mineral state is known as fluorspar or fluorite. Calcium fluoride itself may be disposed of in landfills without any additional treatment.

As an alternative to the above disposal method, a waste disposal firm with which Union Carbide Corporation has a national service contract has been contacted and has submitted a proposal for the neutralization, detoxification and ultimate disposal of the waste. This waste disposal firm, SCA Chemical Services Inc., Earthline Division, Newark, New Jersey, EPA Identification Number NJD 089216790 is permitted to operate as a treatment storage and disposal facility in the State of New Jersey.

I believe the above information to be both true and correct to the best of my knowledge.

Thomas C Ahlers

Thomas C. Ahlers
Region EPA Coordinator
Union Carbide Corporation,
Linde Division

September 7, 1982

Mr. R. S. Pender
Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, NY 10591

Re: Food Additive Petition No. 8B3394

Dear Mr. Pender:

This will acknowledge receipt of your submission dated August 23, 1982 supplementing information contained in the above referenced food additive petition.

This information has been incorporated into our petition jackets and further action awaits our scientific review and evaluation.

Sincerely yours,

Brenda F. Pinch
Petitions Control Assistant
Division of Food & Color Additives
Bureau of Foods

(b) (5)



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September 28, 1982

Mr. Reginald S. Pender
Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, NY 10591

Re: FAP No. 8B3394

Dear Mr. Pender:

This is in reference to your petition, FAP 8B3394, proposing that the food additive regulations be amended to provide for the safe use of fluorinated polyethylene in producing, manufacturing, processing, preparing, packaging, transporting or holding food.

The subject petition has been accepted for filing. The date of this letter is the date of filing of your petition. If we are not able to complete our review of the petition within ninety (90) days of the date of this letter, (December 28, 1982), we will inform you by letter and extend the review for up to 90 additional days. Further action awaits completion of the scientific review.

Sincerely yours,

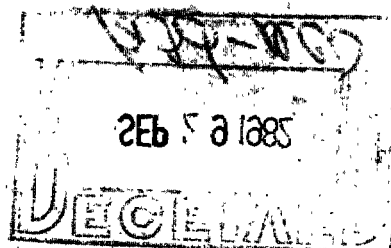
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Julius Smith
Petitions Control Branch, HFP-334
Division of Food and Color Additives
Bureau of Foods

(b) (5)



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Memorandum

Date Oct. 6, 1982

From Food Additive & Animal Drug Chemistry Evaluation Branch, HFF-458

Subject FAP 8B3394 - Union Carbide Corp. (UCC).
Submission dated 8-23-82.

To Petitions Control Branch, HFF-334
Attn: J. Smith

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DCH's 2-8-79 memo discussed numerous deficiencies with this petition. UCC's current submission addresses these deficiencies.

(b) (4)



Nitrogen gas is the only inert gas diluent used for food contact applications. The proposed regulation has been revised to replace the phrase "... in combination with other gases such as nitrogen as inert diluents ..." with "... in combination with gaseous nitrogen as an inert diluent..."

(b) (4)



At this time UCC does not seek to have included in the regulation a provision for an irradiation step.

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Concentration of fluoride ion in the daily diet

DCH's 6-7-78 memo listed fluoride migration levels for non-irradiated containers as follows:

H ₂ O	1.03 ppm
50% Ethanol	.68
3% Acetic acid	.40
n-Heptane	.041

If it is assumed that all food contact polyolefin is fluorinated by UCC's process, the concentration of fluoride ion in the daily diet becomes:

$$0.328[(0.67)(1.03) + (.01)(.40) + (.01)(.68) + (0.31)(0.041)] = 0.23 \text{ ppm} \quad \sim 69 \frac{\text{mg}}{\text{day}}$$

As pointed out in the same DCH memo, no polymerically bound fluorine could be detected in the water extracts. The polymeric extractives found in solution have been ascribed to the usual low molecular weight polyolefin extractives.

DCH has no further questions.

Michael T. Flood

Michael T. Flood, Ph.D.

(b) (5)



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Memorandum

Date November 4, 1982

From Food Additives Evaluation Branch (HFF-156)

Subject Safety Evaluation of Fluorinated Polyethylene for Food and/or Drug Contact Use Applications; Chemistry Memo, 10-6-82; Submission of August 25, 1982.

To Mr. Julius Smith
Petitions Control Branch (HFF-334)

FOOD ADDITIVE PETITION No. 8B-3394

Union Carbide Corporation
Old Saw Mill Road
Tarrytown, N.Y. 10591
AF 15-522

This petition was initially received in March 1978 and requests an amendment permitting Fluorinated Polyethylene for food contact a/o storage items. It was not accepted for filing at that time. In their initial review the Chemists (memo of P.S. Schwartz/J. Smith, June 7, 1978) requested additional information on the manufacturing process and an analysis of total extractives by an independent laboratory. No comments were offered by D.T. at that time. A further submission was made in October 1978. Division of Toxicology (J.C. Edwards/T.R. Carson/J. Smith memo of November 9, 1978) noted that no toxicity data had been submitted and that the identity of the low molecular weight fraction was not discussed, and therefore D.T. found that the petition was not suited for filing.

Division of Toxicology (J.H. Khalsa/J. Smith, March 12, 1979) again reviewed the petition and found it not suitable for filing, because of the lack of a rationale for safety.

Chemical Identity

No chemical formula is provided.

The process is described as producing a surface modified polyethylene by the action of fluorine gas in combination with inert diluents (N₂) such action leaving the bulk of the polymer unchanged. The depth of surface affected is stated to be [redacted]. The surface of the polymer is modified by the treatment. Fluorine gas is stated to be used in concentrations not in excess of amounts required to achieve the intended technical effect. Maximum extractible fractions and maximum soluble fractions shall not exceed those of polyethylene (Schwartz/Smith, June 7, 1978).

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Migrants

According to the Chemists residual (b) (4)

The chemists state that migration of fluoride is as follows:

<u>Solvent</u>	<u>Level</u>
H ₂ O	1.03 ppm
50% Ethanol	0.68 ppm
3% Acetic Acid	0.40 ppm
n-heptane	0.041 ppm

In their calculation of the migration of fluoride, that might be added to the daily diet, the Chemists assume that all food contact polyolefin will be fluorinated by the process. They calculate the concentration of fluoride ion added to the daily diet as 0.23 ppm. The other migrants are those which would ordinarily be found with exposure to polyethylene.

Toxicology

In the submission of August 25, 1982 petitioner addresses the possible migration of organic and inorganic fluorides, questions which are discussed by the Chemistry memoranda. Organic fluorides were demonstrated to be absent. The petitioner then compares the level of fluoride which may migrate from a food contact surface to that in a fluoridated tooth paste and to that used in water treatment programs. No toxicity data are presented.

Discussion

Since the treatment of polyethylene with fluorine gas is said to produce only a surface reaction on the polymer, we wonder whether the additive to be regulated should be fluorine.

The predominant migrant found in aqueous extracts is inorganic fluoride. Organic migrants are said to be identical with those that would be formed from untreated polyethylene, which is already regulated. No organic fluoride is said to migrate. The toxicology of fluoride ion has been well studied. A particularly comprehensive summary is given in IARC (International Agency for Research on Cancer) Vol 27 pp. 237-303, 1982. The data in this latter review have been evaluated by a committee of experts.

The pages relevant to the toxicity of fluoride ion are attached. The report states that chronic administration to rats of 3.8 mg/kg fluoride ion in food and drinking-water results in changes in the teeth and liver and functional changes in kidneys. This may be considered a minimal toxic level. According to Lehman's Tables (Appraisal of Safety of Chemical in Food, Drugs, and Cosmetics, Assoc. of Food and Drug Officials of the U.S., 2nd printing, 1965, frontispiece) this is equivalent to 76 ppm in the diet of a rat or to 146 ppm for man. The IARC monograph further notes the following order of toxicity of fluoride ion for man:

<u>Fluoride Level</u>	<u>Effect</u>
2 ppm	mottled enamel
8 ppm	osteosclerosis
20-80 mg/day	crippling fluorosis
50 ppm	thyroid changes
100 ppm	growth retardation
125 ppm	kidney changes

Thus addition of 0.2 ppm of fluoride ion (F-) to the daily dietary is without consequence toxicologically.

We are concerned, however, with the possible formation and migration of small amounts (b) (4) and of other possibly toxic low molecular weight fluoridated organic compounds. (b) (4)

(b) (4)

the possibilities discussed above. In the absence of such information we would require petitioner to conduct toxicity studies on aqueous extracts of the fluoridated polymer.

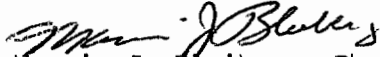
Conclusion

We ask whether the additive to be regulated is actually fluorine gas to treat the surface of polyethylene polymers. The migration data appear to establish fluoride ion and usual low molecular weight extractives of polyethylene as the migrants in food simulating solvents. According to the Chemists the aqueous extracts (water, 50% ethanol, 3% acetic acid extracts) are composed of fluoride ion with trace amounts of low molecular weight oligomers of polyethylene, which are found after extraction of non-fluoridated polyethylene.

Page 4 - Mr. Julius Smith

We ask the chemists to address the question of possible formation of
(b) (4)

In the absence of such information
we would require petitioner to conduct toxicity studies on extracts of
the fluoridated polymer.


Marvin J. Bleiberg, Ph.D.

Attachment

(b) (5)



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Sample matrix	Sample preparation	Assay procedure ^a	Limit of detection	Reference
Sodium silico-fluoride	React with thorium nitrate in presence of sodium alizarine sulphate	T	not given	Koicheva (1974)
Air	Draw through filter; place filter in micro-diffusion vessel with alcoholic sodium hydroxide and distilled water-silver perchlorate-perchloric acid mixture; bake; wash with water; add acetic acid buffer	ISE ^b	0.016 mg/m ³	National Institute for Occupational Safety & Health (1975)
Water	Add to acetic acid buffer	ISE	not given	Harwood (1969)
Tooth enamel	Embed tooth in resin; bombard with γ-ray emissions	CPA	not given	Baljet-Stroobants & Vreven (1979)
	Polish; embed in resin	EMA	not given	Lyon & Hefferren (1970)
	Immerse in perchloric acid; add sodium 2-(para-sulphophenyl-azo)-1,8-dihydroxynaphthalene	C	not given	Lyon & Hefferren (1970)
Urine	Dilute with acetic acid buffer	ISE ^b	0.02 mg/l	National Institute for Occupational Safety & Health (1975)

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^a Abbreviations: ISE, ion-specific electrode; NAA, neutron activation analysis; GC/FID, gas chromatography with flame ionization detection; T, titration; CPA, charged-particle activation; EMA, electron microprobe analysis; C, colorimetry

^b Specific to fluoride ion

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3. Biological Data Relevant to the Evaluation of Carcinogenicity

IARC Vol 27
pp 271-303

3.1 Carcinogenicity studies in animals¹

Oral administration

Mouse: Groups of 54 male and 54 weanling female Swiss CD1 mice were given 10 mg/l sodium fluoride in doubly deionized drinking-water for life, to give a dose of about 70 µg/day fluorine. An equal number of animals served as matched controls. No fluorine was detected in the diet of the animals. Dead animals were weighed and necropsied, gross lesions were recorded, and visible tumours and tissues were examined histologically. The body weight of males was not affected, but that of females was somewhat increased when compared with the corresponding controls. Males given sodium fluoride survived one to two months longer than controls; the life spans of treated and control female mice were similar. Tumours were observed in 24/71 control and 22/72 treated mice, in similar locations and of similar types (Kanisawa & Schroeder, 1969). [The sexes of the animals in which the tumours occurred were not given.]

A group of 50 female DBA mice, seven to ten weeks of age, were fed 900 mg/kg of diet sodium fluoride until the surviving animals were 97-100 weeks of age. An equal number of mice fed a diet without addition of sodium fluoride served as matched controls and were observed for the same period. The treatment resulted in drastic reductions in body weight. Mammary gland carcinomas occurred in 37/47 controls and in 20/40 treated animals. The mean age at appearance of the first tumour was 71 ± 2.3 weeks in controls and 76 ± 3.5 weeks in treated mice (Tannenbaum & Silverstone, 1949).

Groups of 94 C3H and 46 DBA female mice, four to twelve months of age, were given 0.4, 1.0 or 4.0 mg/l sodium fluoride in distilled drinking-water for seven to twelve months. Groups of 96 C3H and 45 DBA female mice were given pure distilled water and served as matched controls. All animals in this series (both treated and control) were also fed a diet containing 20-38 mg/kg fluorine. Other groups, of 65 and 36 C3H mice and 66 and 66 DBA mice, two to nine months of age, received 1.0 and 10.0 mg/l, respectively, sodium fluoride in distilled water for 10-17 months. Groups of 64 C3H and 66 DBA mice served as matched controls. All animals in this second series were fed a mixed-grain diet containing a negligible amount of fluorine. The percentages of deaths due to mammary gland carcinomas were 54% in the controls and 59% in all the experimental groups combined. Among the mice that received 10.0 mg/l fluoride, 63% died of mammary gland carcinomas, compared with 50% of controls (Taylor, 1954). [The Working Group noted that no distinction with regard to tumour incidence was made between the two strains, and that the studies were, in general, inadequately reported.]

¹ The Working Group was aware of a study in progress to assess the carcinogenicity of sodium fluorides in mice and rats by oral and inhalation administration, by injection and by skin painting (Toxicology Information Subcommittee, 1981).

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3.2 Other relevant biological data

(a) *Experimental systems*

Toxic effects

A number of reviews are available on the toxic effects of inorganic fluorides (Eager, 1969; WHO, 1970; Marier & Rose, 1971; Shupe, 1971; Shupe *et al.*, 1972; Taves, 1979).

Data on the acute toxic doses of inorganic fluorides are summarized in Table 13. Acute toxic effects in animals include severe damage to the kidney, gut and liver (Segreto *et al.*, 1961; Taylor *et al.*, 1961a; Shupe, 1971; Limet *et al.*, 1975).

The sustained ingestion of excessive quantities of soluble and insoluble inorganic fluorides induces progressive changes in the teeth and skeleton in all species studied. These changes include dental fluorosis, osteoporosis, osteosclerosis, hyperostoses, osteophytosis and osteomalacia (Shupe *et al.*, 1972). Such effects were seen in cattle whose bones contained more than 5000 mg/kg dry weight fluoride (Marier & Rose, 1971).

The 30-day lethal dose of fluoride in drinking-water of rats was 205 mg/l (Taylor *et al.*, 1961b). Chronic administration to rats of >3.8 mg/kg fluoride (as sodium or stannous fluoride) daily in food and drinking-water resulted in changes in the teeth and liver and structural and functional changes in the kidneys (Jankauskas, 1974; Lim *et al.*, 1975; Roman *et al.*, 1977).

Other organs that may be affected by high levels of fluoride ion (e.g., i.p. administration of 406 mg sodium fluoride over 15 days) are the thyroid, adrenals and pancreas (Ogilvie, 1953; Makhni *et al.*, 1979). A daily intake of fluoride ion too small to give rise to dental changes does not appear to interfere with growth or to lead to pathological changes in the kidneys or other organs (Heyroth, 1952; Lim *et al.*, 1975; Schlatter, 1978).

Effects on reproduction and prenatal toxicity

Fetal serum concentrations of fluoride ion are below or similar to maternal serum concentrations in farm animals (Ericsson & Malmnas, 1962; Bawden *et al.*, 1964; Zipkin & Babeaux, 1965; Shupe *et al.*, 1972).

High i.p. doses of stannous fluoride (≥ 10 mg/kg bw) were reported to cause varying degrees of embryoletality and teratogenicity in groups of five to seven mice (Stratmann, 1979). [The Working Group noted the small sizes of the groups.]

According to Messer *et al.* (1973), fluoride is essential for reproduction; when the intake of female mice was restricted to 0.1-0.3 mg/l in the drinking-water, infertility increased.

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Table 13. LD₅₀ values in experimental animals for some inorganic fluorides

Compound	Species (strain)	Route of administration	LD ₅₀ (mg/kg bw F)	Reference
Sodium fluoride	Mouse (Swiss white) ^b	oral ^c	44.3	Lim et al. (1978)
	Mouse (Swiss white)	i.p.	17.2	Lim et al. (1978)
	Mouse	oral	46.0	Leone et al. (1956)
	Mouse	i.v.	23.0	Leone et al. (1956)
	Rat (Rochester) ^b	oral ^c	51.6	Lim et al. (1978)
	Rat	oral	32.0	Shourie et al. (1950)
	Rat (Rochester)	i.v. ^d	11.8 ^e	Taylor et al. (1961a)
	Rat (Rochester)	i.p.	24	Stokinger (1949)
Stannous fluoride	Mouse (Swiss white)	oral ^c	25.5	Segreto et al. (1961)
	Mouse (Swiss white) ^b	oral	31.2	Lim et al. (1978)
	Rat (Rochester) ^b	oral ^{c, f}	45.7	Lim et al. (1978)
Sodium monofluorophosphate	Mouse (Swiss white) ^b	oral ^c	93.9	Lim et al. (1978)
	Rat	oral	75.0	Shourie et al. (1950)

^a Calculated from mortality data at 24 h. Values have been rounded to the nearest decimal.

^b Animals fasted but given normal access to water for 24 h before treatment

^c Administered *via* stomach tube under light ether anaesthesia

^d The toxicity of intraperitoneally administered sodium fluoride was also studied, but the LD₅₀ was not computed. It was, however, reported to be similar to that with i.v. administration.

^e Mortality at 30 days

^f Administered in an aqueous glycerol (5.0 M)-tartaric acid (0.01 M) solution to prevent hydrolysis and precipitation of tin salts

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However, impaired reproductive performance has also been reported in mice, rats and cattle after intake of large amounts of fluoride, e.g., 100 mg/l in the drinking-water (Cass, 1961; Hodge & Smith, 1965; Messer *et al.*, 1973).

Absorption, distribution, excretion and metabolism

Fluoride ion is rapidly and extensively absorbed from the gut (see, e.g., Cremer & Buttner, 1970). In rats, absorption of sodium fluoride, sodium silicofluoride, sodium monofluorophosphate and stannous fluoride is similar (Wallace-Durbin, 1954; Perkinson *et al.*, 1955; Ericsson & Ullberg, 1958; Shupe *et al.*, 1972; Andreas *et al.*, 1978). Formation of complexes with cations such as Ca, Fe, Mg and Al decreases absorption of fluoride ion (Largent, 1954; Hodge, 1961; Deshpande & Bestor, 1964; Shupe *et al.*, 1972).

Fluoride is transported in the blood in the free rather than the protein-bound form (Chen *et al.*, 1956); it is distributed rapidly throughout all soft tissues but is not accumulated (Wallace-Durbin, 1954; Armstrong & Singer, 1966). It is generally accepted that the fluoride ion is of principal importance in the toxicology of inorganic fluorides (Hodge, 1961).

Excretion occurs mainly *via* the kidneys; renal clearance is greater than that of chloride (Smith *et al.*, 1955; Chen *et al.*, 1956; Carlson *et al.*, 1960a) and is pH-dependent. Thus, tubular reabsorption is increased and clearance decreased when the urine is acidic (Whitford *et al.*, 1976; Whitford & Pashley, 1979). Little fluoride seems to be excreted into the milk (e.g., 0.2% of an i.v. dose in a cow) (Perkinson *et al.*, 1955).

Fluoride accumulates in bones and teeth; and in a three-month experiment in rats, 25-35% of ingested fluoride was retained in the calcified tissues, independent of the concentration of fluoride in the drinking-water (1-100 mg/l) (Taylor *et al.*, 1961b). When fluoride was withdrawn from the drinking-water of rats, the fluoride content of the bones decreased by 44% within the first eight weeks and more slowly thereafter (Miller & Phillips, 1953).

Effects on intermediary metabolism

Fluoride can inhibit a number of enzymes *in vitro*, including cholinesterase (Eager, 1969), DNA polymerase (Hellung-Larsen & Klenow, 1969), and enzymes (such as rat liver microsomal esterases) that are involved in the metabolism of carcinogens (Irving, 1966) and of glycogen (Zebrowski *et al.*, 1964). In intact cells, fluoride is known to inhibit the glycolysis pathway and protein synthesis (Vesco & Colombo, 1970).

Administration of fluoride to animals can lead to reductions in the levels of some enzymes, such as serum alkaline phosphatases and esterases (Riekstniece *et al.*, 1965; Ferguson, 1971).

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Mutagenicity and other short-term tests

Sodium fluoride did not induce reverse mutations in *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 or TA100 when tested at up to 500 µg/plate in the absence, or at up to 2000 µg/plate in the presence, of a liver activation system from Aroclor 1254-induced rats. It did not induce gene conversion in *Saccharomyces cerevisiae* strain D4 in the same study (Martin *et al.*, 1979).

No sex-linked recessive lethals were induced in *Drosophila melanogaster* when sodium fluoride was administered by injection of a 10^{-3} M solution (Mukherjee & Sobels, 1968) or when adults were fed 0.025% in a honey solution (Mendelson, 1976). However, Mitchell & Gerdes (1973) reported a significant enhancement in the frequency of sex-linked recessive lethals after treatment with concentrations of 6% sodium fluoride or 25% stannous fluoride. [The Working Group questioned whether sodium fluoride is soluble at the levels used, and noted the unusually low spontaneous mutation frequencies reported.]

Sodium monofluorophosphate did not induce dominant lethal mutations in mature sperm or oocytes of *Drosophila* fed concentrations of up to 60 mM for as long as 36 h (Buchi, 1977).

Feeding of sodium fluoride to mice at concentrations of up to 50 mg/kg of diet for seven generations did not induce chromosomal aberrations or increase the frequency of sister chromatid exchanges in bone marrow (Kram *et al.*, 1978). In two other experiments with mice, Martin *et al.* (1979) found no evidence of chromosomal damage in either bone-marrow or testicular cells. In the first of these experiments, Swiss-Webster mice were fed for two years on a low-fluoride diet (0.5 mg/kg) and given drinking-water containing either 0 or 50 mg/l sodium fluoride. In the second experiment, BALB/c male mice were given the same low-fluoride diet and up to 100 mg/l sodium fluoride in their drinking-water for six weeks. Earlier, it had been claimed that chromosomal changes were induced in testicular and bone-marrow cells of BALB/c mice with doses as low as 1 mg/l sodium fluoride in drinking-water for three to six weeks (Anon., 1976; Mohamed & Chandler, 1977). The validity of this finding has been questioned by Martin *et al.* (1979).

Cytological changes have been observed in the chromosomes of cow and ewe oocytes when cultured in the presence of up to 0.1 and 0.2 mg/ml sodium fluoride, respectively and in cultures of mouse oocytes at concentrations below 0.4 mg/ml. The effects were not dose-related. No cytogenetic effects were induced in oocytes of mice exposed to sodium fluoride as a single, acute dose (500 µg intravenously) or chronically (250 µg subcutaneously daily for 16 days) (Jagiello & Liu, 1974).

No increase in chromosomal aberrations was observed in human lymphocytes treated with up to 3×10^{-3} M (Voroshilin *et al.*, 1973) or up to 10 mg/l sodium fluoride (Kralisz & Szymaniak, 1978).

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Genetic effects, including anaphase lagging, bridges, tetraploidy, multipolar anaphases and increase in the frequency of abnormal mitotic figures, have been induced in several plant species by sodium fluoride (Mohamed *et al.*, 1966; Hakeem & Shehab, 1970; Mouftah & Smith, 1971; Bale & Hart, 1973a,b; Galal & Abd-Alla, 1976; Temple & Weinstein, 1978).

(b) *Humans*

Toxic effects

(i) *Acute toxicity*

Immediate effects of the ingestion of a toxic dose of a soluble inorganic fluoride occur in the gut; these include vomiting, abdominal pain and diarrhoea. The severity of the symptoms is dose-related (Princi, 1960; Hodge & Smith, 1972; Hoffman *et al.*, 1980; Spoerke *et al.*, 1980). These effects have also been reported to occur with lower doses (1-1.2 mg/day in tablet form) in some particularly sensitive individuals (Feltman & Kosel, 1961; Shea *et al.*, 1967).

Convulsions have been observed following absorption of 0.2-27.5 g fluoride (Roholm, 1936; Princi, 1960), and repeated ventricular fibrillation after ingestion of 120 g sodium fluoride (Abukurah *et al.*, 1972). Lethal doses of inorganic fluoride lie between 50 and 225 mg/kg bw (Smith & Hodge, 1959; Schlatter, 1978; Spoerke *et al.*, 1980). In fatal cases of fluoride poisoning, death is usually due to respiratory paralysis (Spoerke *et al.*, 1980). Autopsy shows acute congestion of the abdominal viscera, swelling of the liver and kidneys, tubular necrosis, haemorrhages in the lungs and dilatation of the right chambers of the heart (Lidbeck *et al.*, 1943).

Allergic responses to fluoride have been reported, although the role of fluoride in these responses has been questioned (Shea *et al.*, 1967; Zanfagna, 1976).

(ii) *Chronic toxicity*

With chronic exposure, toxic effects are seen in teeth, bones, kidneys, the reproductive system and blood (Schlatter, 1978). Smith & Hodge (1959) related fluoride intake to toxic effects as follows (Table 14):

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Table 14. Effects of various fluoride concentrations in water and food, or daily intake

Fluoride level	Effect
≥2 ppm	Mottled enamel
8 ppm	Osteosclerosis
≥20-80 mg/day	Crippling fluorosis
>50 ppm	Thyroid changes
100 ppm	Growth retardation
>125 ppm	Kidney changes

Continuous or intermittent exposure to inorganic fluorides can lead to appreciable accumulation of fluoride in bone and to the development of osteosclerosis and other bone changes (WHO, 1970). However, bone changes consistent with skeletal fluorosis were detected in only 23 cases in a study of 170000 X-ray records (spine and pelvis) of people from communities where the fluoride concentrations in the drinking-water exceeded 0.7 mg/l (Stevenson & Watson, 1957).

In areas of endemic fluorosis and high poverty, the combination of excessive fluoride intake and nutritional insufficiency may lead not only to crippling skeletal malformations (see, e.g., WHO, 1970; Maiya *et al.*, 1977) but also to neurological disorders (Siddiqui, 1955; Singh *et al.*, 1963; Singh & Jolly, 1970) and may be associated with haematological abnormalities (Schlatter, 1978).

In areas of fluorosis in which the fluoride concentration in the drinking-water ranged from 5.0-16.2 mg/l, decreased urea clearance and glomerular filtration rate, together with increased blood urea have been observed (Siddiqui, 1955; Singh *et al.*, 1963). In addition to skeletal changes, an increased incidence of renal calculi has also been reported (Herman, 1955).

Adverse effects of water-borne fluoride (5-13 mg/l) have been reported on the heart (Okushi, 1954; Takamori *et al.*, 1956; Jansen & Thomson, 1974; see also Waldbott, 1961). Earlier reports of dysfunction of the thyroid (Wilson, 1941; Spira, 1944, 1946; Murray *et al.*, 1948) have not been confirmed (e.g., Singh *et al.*, 1963; Latham & Grech, 1967).

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Effects on reproduction and prenatal toxicity

After injection of ^{18}F , fetal serum concentrations did not exceed 25% of that in the maternal blood (Ericsson & Malmnas, 1962). Fluoride that crosses the placenta is deposited in fetal bones and teeth in amounts that increase with the age of the fetus (Brzezinski *et al.*, 1960) and with the fluoride intake of the mother (Gedalia *et al.*, 1964). Mottled dental enamel has been found in the teeth of children whose mothers drank water containing 12-18 mg/l fluoride (Smith & Smith, 1935). The fluoride content of maternal milk ranges from <0.1 to 0.2 mg/l. It increases by about 15-40% with daily supplements of 5 mg fluoride in the diet or drinking-water (WHO, 1970).

Early reports of an association between the presence of naturally occurring fluorides in water supplies and cases of Down's syndrome, ascertained from records of specialized institutions (Rapaport, 1956) and from birth and death certificates (Rapaport, 1959), have not been confirmed in later studies in which there was more complete ascertainment and/or consideration of mother's age (Berry, 1958; Needleman *et al.*, 1974; Erickson *et al.*, 1976; Erickson, 1980). No association with other congenital malformations has been observed (Erickson *et al.*, 1976).

Absorption, distribution, excretion and metabolism

This field has been covered in a number of reviews (WHO, 1970; National Institute for Occupational Safety & Health, 1975; National Research Council, 1977). Fluoride ion is absorbed rapidly: 96-97% from solutions of sodium and calcium fluoride, and 62% from calcium fluoride in solid form (Largent, 1961). Absorption begins in the stomach and continues in the duodenum and jejunum (Schlatter, 1978). It may be affected by levels of both dietary organic material (protein and fat) and ions (Ca^{++} , Mg^{++} , PO_4^-) (Waldbott, 1961).

Fluoride is excreted mainly in the urine; however, excretion in sweat may account for 25% of total excretion, and for up to 50% when sweating is excessive (McClure *et al.*, 1945; Crosby & Shepherd, 1957).

Fluoride levels found in human tissues are given in section 2.2; 96-97% of fluoride in human plasma is freely diffusible (Carlson *et al.*, 1960b). The rate of skeletal accumulation (retention) of fluoride is influenced by the amount ingested and the amount already accumulated (Largent, 1961). It has been estimated (Myers *et al.*, 1980) that if a person were to move from a high-fluoride (8 mg/l in the drinking-water) to a low-fluoride (<0.3 mg/l) locality, the half-life of the fluoride in his bones would be approximately eight years.

Effects on intermediary metabolism

As in animals (see p. 274), certain enzymes in human tissues are inhibited by fluoride (Frajola, 1960; Abukurah *et al.*, 1972).

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Mutagenicity and chromosomal effects

No data were available to the Working Group.

3.3 Case reports and epidemiological studies of carcinogenicity in humans

Although the Working Group was aware of a number of epidemiological studies on the relation between cancer and occupational exposures to inorganic fluorides concurrently with a variety of other chemicals (e.g., in the aluminium production industry), the only studies reviewed in this section are those which relate to inorganic fluorides in drinking-water. The epidemiological studies considered are summarized in Table 16.

All are descriptive (sometimes called correlational or ecological) studies, in which both exposure and disease are measured in population aggregates. For the purpose of inferring causal relationships, they are generally less satisfactory and contain more sources of error than analytical studies, in which ascertainment of exposure and disease status is made separately for individual people rather than cities or counties (see preamble, p. 16). For example, because of the constant migration in and out of large population centres, the exposures of aggregates that are ascertained at one moment in time refer to a different set of people than do the measures of disease made after a suitable latent period. Variations in disease frequency between the population units may be due to differences in their demographic composition, degree of industrialization, exposure to environmental pollutants, ethnic distribution or life style, to mention only a few possibilities. Since the age-sex-race compositions of populations are often known, it is possible to eliminate or to reduce substantially the bias from this source by the use of appropriately standardized rates. The unexplained variations in the adjusted rates between population units are the appropriate background against which to evaluate the significance of differences among groups of units classified by their exposure. However, because of the small number of such units typically available for study, it is difficult to control adequately for confounding effects. Particular weaknesses which apply to several of the studies considered below are failure to consider each cancer site separately, and failure to account for the variability in rates between population units in the analysis and presentation of results.

Hagan *et al.* (1954) identified 32 US cities with a population in 1950 of 10000 or more, in which the water supplies contained natural fluoride in concentrations of 0.7 mg/l or greater, and which were near 32 cities of similar size with natural fluoride levels of less than 0.25 mg/l which could serve as controls. The total populations were 0.9 million in the high-fluoride cities and 1.3 million in the low. Cancer death rates in 1950, indirectly standardized for age, race and sex by reference to the rates prevailing in the US in 1950, averaged 135.4 per 100000 for high-level cities and 139.1 for low, a difference which is not statistically significant. Equally, there were no differences in mortality from heart disease, intracranial vascular lesions, nephritis or liver cirrhosis. [No attempt was made in this study to consider other characteristics of the sampled cities which might be related to cancer mortality; however, the comparability of rates for other causes of death provides some assurance that no large bias was present.]

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4. Summary of Data Reported and Evaluation

4.1 Experimental data

Sodium fluoride was tested in three experiments in three different strains of mice by oral administration. The available data are insufficient to allow an evaluation to be made.

Sodium fluoride was not mutagenic to *Salmonella typhimurium* or *Drosophila melanogaster* and did not induce gene conversion in *Saccharomyces cerevisiae*.

4.2 Human data

Significant mining of fluor spar (calcium fluoride) started in about 1775. The natural occurrence of some inorganic fluorides and their use in water fluoridation and anti-caries dental products results in widespread exposure of the general population. In addition, the numerous industrial applications of these chemicals result in significant occupational exposure and emissions to the environment.

Only studies on water fluoridation and cancer were reviewed. The relationship between cancer mortality or incidence and both natural and artificial fluoride in drinking-water has been investigated in a large number of descriptive epidemiological studies of population aggregates, carried out in Australia, Canada, New Zealand, Norway, the United Kingdom and the United States. Because of the uneven distribution of natural fluoride in the earth's crust, and the fact that local communities make independent decisions with regard to fluoridation, some of these studies could be viewed roughly as natural experiments. When proper account was taken of the differences among population units, in demographic composition, and in some cases also in their degree of industrialization and other social factors, none of the studies provided any evidence that an increased level of fluoride in water was associated with an increase in cancer mortality.

4.3 Evaluation

The available data are inadequate for an evaluation of the carcinogenicity of sodium fluoride, the only inorganic fluoride tested, in experimental animals.

Variations geographically and in time in the fluoride content of water supplies provide no evidence of an association between fluoride ingestion and mortality from cancer in humans.

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(b) (5)



000191



Memorandum

Date Dec. 21, 1982


From Food Additive & Animal Drug Chemistry Evaluation Branch, HFF-458

Subject FAP 8B3394 - Union Carbide Corp.
DT's request for information dated 11-4-82.

To Petitions Control Branch, HFF-334
Attn: J. Smith

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DT has asked DCH "to address the question of possible formation of
(b) (4)



Our general conclusion is that low molecular weight fluorocarbon-oxygen compounds should not be present in significant quantities.

In rereading this petition we note that the general fluorination process was submitted as a patent. The patent says, in part, "Wash Chamber 72 is an adjunct to the main part of the invention and may not always be needed ... In it, the product is water-washed for a period of several minutes to remove traces of fluorine or HF" (Page 000093). For food contact use we would consider GMP to always include water washing the treated article.

Michael T. Flood

Michael T. Flood, Ph.D.

(b) (5)



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December 23, 1982

Mr. R. S. Pender
Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, NY 10591

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Re: Food Additive Petition No. 8E3394

Dear Mr. Pender:

This letter is to inform you we have extended the scientific review of the above referenced food additive petition for an additional 90 days in accordance with section 409(c)(2) of the Federal Food, Drug, and Cosmetic Act.

Sincerely yours,

Brenda F. Finch
Petitions Control Assistant
Division of Food & Color Additives
Bureau of Foods

(b) (5)



000194



Memorandum

Date January 17, 1983

From Food Additive Evaluation Branch (HFF-156)

Subject Chemistry memo of Dec. 21, 1982 regarding possible reaction products of oxygen with fluorinated polyethylene.

To Petitions Control Branch (HFF-334)
Attn: Dr. Julius Smith

FOOD ADDITIVE PETITION NO. 8B-3394

Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, New York 10591

In reply to concerns raised in our memo of Nov. 4, 1982 (Bleiberg/Smith), Chemistry has reviewed the reactivity and stability of the polymer chain of fluorinated polyethylene. Since fluoridation is a surface phenomenon, the Chemists have concluded that the organic migrants are the usual low molecular weight polyolefin extractives as characterized for the polyolefins already regulated and that inorganic fluoride migration levels in the exaggerated situation that 100% of polyethylene in use will be fluoridated amounts to 0.23 ppm. (memo of Flood/Smith, Oct. 6, 1982). The chemists note the GMP should include water washing at the conclusion of the fluoridation process. The chemists consider the fluoridated polymer to be extremely stable. (b) (4)

We previously noted (Bleiberg/Smith memo of Nov. 4, 1982) that addition of 0.2 ppm fluoride to the food supply is without toxicologic significance. Based on the chemical information available, we have no further questions and concur with regulation of the petition.

Marvin J. Bleiberg
Marvin J. Bleiberg, Ph.D. 1-17-83

(b) (5)

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DEPARTMENT OF HEALTH AND HUMAN SERVICES

FOOD AND DRUG ADMINISTRATION

[DOCKET NO. 83F-0049]

UNION CARBIDE CORP.; FILING OF FOOD ADDITIVE PETITION

AGENCY: Food and Drug Administration.

ACTION: Notice.

SUMMARY: The Food and Drug Administration (FDA) is announcing that Union Carbide Corp. has filed a petition proposing that the food additive regulations be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

FOR FURTHER INFORMATION CONTACT:

Julius Smith,
Bureau of Foods (HFF-334),
Food and Drug Administration,
200 C St. SW.,
Washington, DC 20204,
202-472-5690.

83-134

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The potential environmental impact of this action is being reviewed. If the agency finds that an environmental impact statement is not required and this petition results in a regulation, the notice of availability of the agency's finding of no significant impact and the evidence supporting that finding will be published with the regulation in the FEDERAL REGISTER in accordance with 21 CFR 25.40(c) (proposed December 11, 1979; 44 FR 71742).

Dated: _____

000197

Union Carbide Corporation
Tarrytown, NY 10591

MEMORANDUM OF TELEPHONE CONVERSATIONS

March 1 and 2, 1983

Between: Dr. Michael Flood
FDA/DCH, HFF-458

and: Dr. Jerry C. Smrcek
FDA/PEERS/Environmental Impact Section, HFF-27

Subject: Environmental Considerations for FAP 8B 3394 -
Fluorinated Polyethylene in Food Contact Articles

I called Dr. Flood to discuss the extraction study information in the petition and to find out if it would be possible to calculate the amount of fluoride ion that would be present in the treated polyethylene, the food packaging material.

The petitioner obtained a migration value in water of 1.03 ppm. This level is high when compared to possible toxic levels to organisms of 1.5 ppm noted by researchers. Dr. Flood said that when fluorine is combined with polyethylene a certain portion will be combined with the carbon atoms of the polymer to form a Teflon product. This polymer bound fluorine portion would not be extracted. The rest of the fluorine (as HF) is a residue, which is extracted in water and dissociates into fluoride ions. It is these ions that result in the 1.03 ppm value. In discussing extrapolation of the migration level to exposure levels in the environment, Dr. Flood confirmed that the 1.03 ppm value could be treated as a worst-case concentration. Also, it is highly unlikely that a concentration this high would be present in the environment.

Dr. Flood said he did not know of any way to calculate the amount of flouride ion present in the treated polyethylene. In addition, he said he did not know how much polyethylene would be treated with the fluorine gas. These questions could possibly be answered by calling the petitioner.

Jerry C. Smrchek
Jerry C. Smrchek, Ph.D.

(b) (5)

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Union Carbide Corporation
Tarrytown, NY 10591

MEMORANDUM OF TELEPHONE CONVERSATIONS

March 2 and 7, 1983

Between: Mr. Reginald S. Pender
Research and Development
Union Carbide Corporation
(914)789-2207

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and: Dr. Jerry C. Smrcek
FDA/PEERS/Environmental Impact Section, HFF-27

Subject: Environmental Considerations for FAP 8B 3394 -
Fluorinated Polyethylene in Food Contact Articles

I called Mr. Pender on March 2 to try to obtain information regarding two questions discussed below. He returned my call with answers on March 7.

Question 1 - How much polyethylene will be treated (fluorinated) and marketed on an annual basis by Union Carbide? Mr. Pender said he estimates that (b) [redacted] of polyethylene will be treated and (b) [redacted] pounds of fluorine will be used on an annual basis.

Question 2 - Would it be possible to determine the amount of extractable fluoride ion in the treated polyethylene on an area basis (mg/in²) so as to determine an environmental exposure level? Mr. Pender said he estimates that (b) (4) [redacted] of fluoride ion would be introduced into the environment annually. This value was derived by multiplying (b) (4) [redacted] (maximum fluoride consumed) by (b) (4) [redacted]. He said he had no information on determining an area estimate (mg/in² of fluoride ion.


Jerry C. Smrcek, Ph.D.

(b) (5)
[redacted]

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FINDING OF NO SIGNIFICANT IMPACT

FOR

Food Additive Petition 8B 3394, submitted by Union Carbide Corporation,
which concerns the use of fluorinated polyethylene in food contact
articles.

The approval of this petition will not require the preparation of an
Environmental Impact Statement.

Prepared by: *Jerry C. Smrcek*
Jerry C. Smrcek, Ph.D., Ecologist
Environmental Impact Section

Date: 3/10/83

Approved by: *Buzz L. Hoffman*
Buzz L. Hoffman, Ph.D., Chief
Environmental Impact Section

Date: 3/10/83

000200

FINDING OF NO SIGNIFICANT IMPACT

FOR

Food Additive Petition 8B 3394, submitted by Union Carbide Corporation, which concerns the use of fluorinated polyethylene in food contact articles.

The petitioner submitted an Environmental Impact Analysis Report (EIAR) on the requested action in the format specified in 21 CFR 25.1(j). We conclude that approval of this petition will not significantly affect the quality of the human environment and therefore will not require the preparation of an Environmental Impact Statement. The basis for this conclusion is as follows:

1. The fluorine gas will be used to alter the surface of the polymer polyethylene, thereby reducing the latter's permeability to gases (CO_2 , O_2) and reducing resistance to solvents (hexane, xylene). The fluorine gas will be used at a concentration of (b) (4) volume in combination with nitrogen (N_2) gas as an inert diluent. (b) (4) of fluorine are expected to be used annually.
2. Potential environmental introductions of the gas during its incorporation with polyethylene are expected to be minimal. According to the petitioner, the reaction and incorporation occurs in a reduced pressure closed system of atmospherically sealed chambers. All reaction gas, diluent gas, and gaseous by-products (hydrogen fluoride and fluorine gas) of the process are handled and transferred at reduced pressure in this closed system to a scrubber section. These gases are converted to products such as calcium fluoride that, according to the petitioner, are safe, easily handled, and can be disposed of in landfills. The treated polyethylene will be removed from the reaction process chamber by remote, automatic means so that worker exposure to the reaction treatment gases or by-products will not occur. A citation of, and statement of compliance with, applicable emission requirements was provided by the petitioner.
3. Potential environmental introductions of the fluorinated polyethylene during use as food contact articles and due to disposal of these articles are expected to be minimal. Extraction studies were conducted by the petitioner with the fluorinated polyethylene in xylene solvents. No detectable fluorine bound species were found by the petitioner to be removed as a xylene soluble product. Also, when extraction studies into a food simulating solvent (water) were conducted a maximum level of 1.03 ppm inorganic fluoride ion was found (memorandum of October 6, 1982 from Dr. M. T. Flood, DCH, HFF-458). No polymerically bound fluorine was detected in the water extracts. It is highly unlikely that the 1.03 ppm migration level would be present in water in the receiving environment (e.g., near a disposal site) due to the proposed use, and this was confirmed by Dr. Michael T. Flood, DCH, HFF-458 (telephone conversation, March 2, 1983).

Further, a worst-case concentration of the additive (fluoride ions) that could be leached from landfill disposal sites was calculated to be less than 0.007 ppm.

4. With regard to the toxicity of the additive, concentrations as low as 1.5 mg/l of fluoride ion have been found to affect the hatching of fish eggs and 2.3 mg/l (as sodium fluoride) was found to be lethal to rainbow trout, Salmo gairdneri (cited in Water Quality Criteria, 1972, National Academy of Sciences, Committee on Water Quality Criteria). At the anticipated levels of environmental exposure, we would expect fluoride ions to be non-toxic to organisms in the receiving environment.

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Union Carbide Corp.; Filing of Food
Additive Petition

8B3394 - Smith

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4. Persons initialing documents (or persons designated by them) shall fill in dates of receipt and release of document in applicable spaces on this route slip.
5. All FR documents in final form must bear initials of GC before forwarding for signature to the Commissioner, the Deputy Commissioner, or the Associate Commissioner for Compliance.
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(b) (5)

4160-01

DEPARTMENT OF HEALTH AND HUMAN SERVICES

FOOD AND DRUG ADMINISTRATION

[DOCKET NO. 83F-0049]

UNION CARBIDE CORP.; FILING OF FOOD ADDITIVE PETITION

AGENCY: Food and Drug Administration.

ACTION: Notice.

SUMMARY: The Food and Drug Administration (FDA) is announcing that Union Carbide Corp. has filed a petition proposing that the food additive regulations be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

FOR FURTHER INFORMATION CONTACT:

Julius Smith,
Bureau of Foods (HFF-334),
Food and Drug Administration,
200 C St. SW.,
Washington, DC 20204,
202-472-5690.

83-134

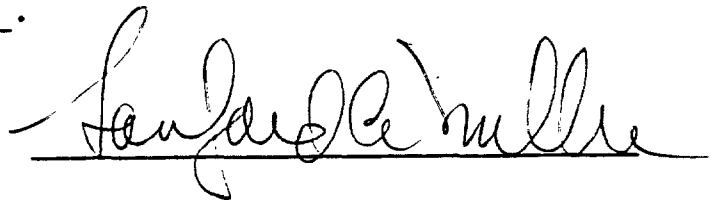
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SUPPLEMENTARY INFORMATION: Under the Federal Food, Drug, and Cosmetic Act (sec. 409(b)(5), 72 Stat. 1786 (21 U.S.C. 348(b)(5))), notice is given that a petition (FAP 8B3394) has been filed by Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that Part 177 (21 CFR Part 177) be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

The potential environmental impact of this action is being reviewed. If the agency finds that an environmental impact statement is not required and this petition results in a regulation, the notice of availability of the agency's finding of no significant impact and the evidence supporting that finding will be published with the regulation in the FEDERAL REGISTER in accordance with 21 CFR 25.40(c) (proposed December 11, 1979; 44 FR 71742).

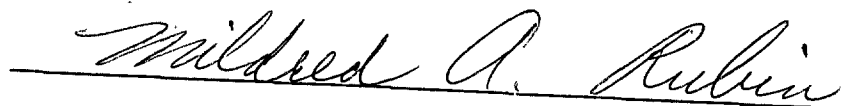
Dated: 3/18/83.

MAR 18 1983



Sanford A. Miller
Director, Bureau of Foods

CERTIFIED TO BE A TRUE COPY OF THE ORIGINAL



J. SMITH
FAP 8B3394

NOTICES

BEST ORIGINAL COPY

[Docket No. 83F-0049]

Union Carbide Corp.; Filing of Food Additive Petition

AGENCY: Food and Drug Administration.

ACTION: Notice

SUMMARY: The Food and Drug Administration (FDA) is announcing that Union Carbide Corp. has filed a petition proposing that the food additive regulations be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

FOR FURTHER INFORMATION CONTACT: Julius Smith, Bureau of Foods (HFF-334), Food and Drug Administration, 200 C St. SW., Washington, DC 20204, 202-472-5690.

SUPPLEMENTARY INFORMATION: Under the Federal Food, Drug and Cosmetic Act (sec. 409(b)(5), 72 Stat. 1786 (21 U.S.C. 348(b)(5))), notice is given that a petition (FAP 8B3394) has been filed by Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that Part 177 (21 CFR Part 177) be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

The potential environmental impact of this action is being reviewed. If the agency finds that an environmental impact statement is not required and this petition results in a regulation, the notice of availability of the agency's finding of no significant impact and the evidence supporting that finding will be published with the regulation in the **Federal Register** in accordance with 21 CFR 25.40(c) (proposed December 11, 1979; 44 FR 71742).

Dated: March 18, 1983.

Sanford A. Miller,
Director, Bureau of Foods.

[FR Doc. 83-7837 Filed 3-28-83; 8:45 am]
BILLING CODE 4160-01-M

DEPARTMENT OF HEALTH AND HUMAN SERVICES

FOOD AND DRUG ADMINISTRATION

21 CFR PART 177

[DOCKET NO. 83F-0049]

INDIRECT FOOD ADDITIVES: Polymers

AGENCY: Food and Drug Administration.

ACTION: Final rule.

SUMMARY: The Food and Drug Administration (FDA) is amending the food additive regulations to provide for the safe use of fluorine treated polyethylene as a food-contact surface.

This action is in response to a petition filed by Union Carbide Corp.

DATES: Effective (insert date of publication in the FEDERAL REGISTER); objection by (insert date 30 days after date of publication in the FEDERAL REGISTER).

ADDRESS: Written objections to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT:

Julius Smith,
Bureau of Foods (HFF-334),
Food and Drug Administration,
200 C St. SW.,
Washington, DC 20204,
202-472-5690.

SUPPLEMENTARY INFORMATION: In a notice published in the FEDERAL REGISTER of March 29, 1983, (48 FR 13098), FDA announced that a petition (FAP 8B3394) had been filed by Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that the food additive regulations be amended to provide for the safe use of fluorine treated polyethylene as a component of food-contact surfaces.

FDA has evaluated data in the petition and other relevant material and concludes that the proposed food additive use is safe and that the regulations should be amended as set forth below. In accordance with §171.1(h) (21 CFR 171.1(h)), the petition and the documents that FDA considered and relied upon in reaching its decision to approve the petition are available for inspection at the Bureau of Foods (address above) by appointment with the contact person listed above. As provided in 21 CFR 171.1(h)(2), the agency will remove from the documents any materials that are not available for public disclosure before making the documents available for inspection.

The agency has considered the potential environmental effects of this action and has concluded that the action will not have a significant impact on the human environment and that an environmental impact statement is not required. The agency's finding of no significant impact and the evidence supporting that finding may be seen in the Dockets Management Branch (address above), between 9 a.m. and 4 p.m., Monday through Friday.

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List of Subjects in 21 CFR Part 177

Food additives, Polymeric food packaging.

Therefore, under the Federal Food, Drug, and Cosmetic Act (secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348)) and under authority delegated to the Commissioner of Food and Drugs (21 CFR 5.10) and redelegated to the Bureau of Foods (21 CFR 5.61 as revised February 4, 1983; 48 FR 5251), Part 177 is amended in Subpart B by inserting a new section to read as follows:

PART 177--INDIRECT FOOD ADDITIVES: POLYMERS

Subpart B - Substances for Use as Basic Components of Single and Repeated Use Food Contact Surfaces.

§177._____ Polyethylene, fluorinated.

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food contact articles in accordance with the following prescribed conditions;

(a) Fluorinated polyethylene food contact articles are produced by modifying the surface of polyethylene articles through action of fluorine gas in combination with gaseous nitrogen as an inert diluent. Such modification shall affect only the surface of the polymer leaving the interior unchanged.

(b) Fluorinated polyethylene articles shall be manufactured from basic resins containing not less than 85 weight-percent of polymer units derived from ethylene and identified in §177.1520 paragraph (a)(2) and paragraph (a)(3). The fluorinated polyethylene articles shall conform to the

specifications and use limitations of §177.1520 paragraph (c)(2.1) and paragraph (c)(3.1).

(c) The finished food contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of §176.170 (c) of this chapter, yields fluoride ion not to exceed 5 ppm calculated on the basis of the volume of food held by the food contact article.

Any person who will be adversely affected by the foregoing regulation may at any time on or before (insert date 30 days after date of publication in the FEDERAL REGISTER) submit to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857, written objections thereto and may make a written request for a public hearing on the stated objections. Each objection shall be separately numbered and each numbered objection shall specify with particularity the provision of the regulation to which objection is made. Each numbered objection on which a hearing is requested shall specifically so state; failure to request a hearing for any particular objection shall constitute a waiver of the right to a hearing on that objection. Each numbered objection for which a hearing is requested shall include a detailed description and analysis of the specific factual information intended to be presented in support of the

objection in the event that a hearing is held; failure to include such a description and analysis for any particular objection shall constitute a waiver of the right to a hearing on the objection. Four copies of all documents shall be submitted and shall be identified with the Dockets Management Branch docket number found in brackets in the heading of this regulation. Received objections may be seen in the above office between the hours of 9 a.m. and 4 p.m., Monday through Friday.

Effective date. This regulation shall become effective (insert date of publication in the FEDERAL REGISTER).

(Secs. 201(s), 409, 72 Stat. 1784-1788 an amended (21 U.S.C. 321(s), 348).).

Dated: _____

(b) (5)



May 5, 1983

Mr. R. S. Pender
Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, NY 10591

Re: Food Additive Petition No. 8B3394

Dear Mr. Pender:

BEST ORIGINAL COPY

Enclosed is a preliminary draft of a regulation which we are considering as a possible response to the above referenced petition.

Your prompt review of the draft and a response will expedite the processing of the petition.

Sincerely yours,

Julius Smith
Petitions Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods

Enclosure

(b) (5)



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DEPARTMENT OF HEALTH AND HUMAN SERVICES

FOOD AND DRUG ADMINISTRATION

21 CFR PART 177

[DOCKET NO. 83F-0049]

INDIRECT FOOD ADDITIVES; POLYMERS

AGENCY: Food and Drug Administration.

ACTION: Final rule.

SUMMARY: The Food and Drug Administration (FDA) is amending the food additive regulations to provide for safe use of fluorine-treated polyethylene as a food-contact surface. This action responds to a petition filed by the Union Carbide Corp.

DATES: Effective (insert date of publication in the FEDERAL REGISTER); objection by (insert date 30 days after date of publication in the FEDERAL REGISTER).

ADDRESS: Written objections to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT:

Julius Smith,
Bureau of Foods (HFF-334),
Food and Drug Administration,
200 C St. SW.,
Washington, DC 20204,
202-472-5690.

SUPPLEMENTARY INFORMATION: In a notice published in the FEDERAL REGISTER of March 29, 1983 (48 FR 13098), FDA announced that a petition (FAP 8B3394) had been filed by the Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that the food additive regulations be amended to provide for safe use of fluorine-treated polyethylene as a component of food-contact surfaces.

In accordance with § 171.1(h) (21 CFR 171.1(h)), the petition and the documents that FDA considered and relied upon in reaching its decision to approve the petition are available for inspection at the Bureau of Foods (address above) by appointment with the information contact person listed above. As provided in § 171.1(h)(2), the agency will delete from the documents any materials that are not available for public disclosure before making the documents available for inspection.

The agency has considered the potential environmental effects of this action and has concluded that the action will not have a significant impact on the human environment and that an environmental impact statement is not required. The agency's finding of no significant impact and the evidence supporting that finding may be seen in the Dockets Management Branch (address above), between 9 a.m. and 4 p.m., Monday through Friday.

List of Subjects in 21 CFR Part 177

Food additives; Polymeric food packaging.

Therefore, under the Federal Food, Drug, and Cosmetic Act (secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348)) and under authority delegated to the Commissioner of Food and Drugs (21 CFR 5.10) and redelegated to the Bureau of Foods (21 CFR 5.61 as revised February 4, 1983; 48 FR 5251), Part 177 is amended in Subpart B by adding new § 177.1615, to read as follows:

PART 177--INDIRECT FOOD ADDITIVES: POLYMERS

§ 177.1615 Polyethylene, fluorinated.

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food-contact articles in accordance with the following prescribed conditions:

(a) Fluorinated polyethylene food-contact articles are produced by modifying the surface of polyethylene articles through action of fluorine gas in combination with gaseous nitrogen as an inert diluent. Such modification shall affect only the surface of the polymer, leaving the interior unchanged.

~~(b)~~ Fluorinated polyethylene articles shall be manufactured from basic resins containing not less than 85 weight-percent of polymer units derived from ethylene and identified in § 177.1520(a)(2) and (3). ^(b) The fluorinated polyethylene articles shall conform to the specifications and use limitations of § 177.1520(c), items 2.1 and 3.1.

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(c) The finished food-contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of § 176.170(c) of this chapter, yields fluoride ion not to exceed 5 parts per million calculated on the basis of the volume of food held by the food-contact article.

Any person who will be adversely affected by the foregoing regulation may at any time on or before (insert date 30 days after date of publication in the FEDERAL REGISTER) submit to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857, written objections thereto and may make a written request for a public hearing on the stated objections. Each objection shall be separately numbered and each numbered objection shall specify with particularity the provision of the regulation to which objection is made. Each numbered objection on which a hearing is requested shall specifically so state; failure to request a hearing for any particular objection shall constitute a waiver of the right to a hearing on that objection. Each numbered objection for which a hearing is requested shall include a

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detailed description and analysis of the specific factual information intended to be presented in support of the objection in the event that a hearing is held; failure to include such a description and analysis for any particular objection shall constitute a waiver of the right to a hearing on the objection. Three copies of all documents shall be submitted and shall be identified with the docket number found in brackets in the heading of this regulation. Received objections may be seen in the office above between 9 a.m. and 4 p.m., Monday through Friday.

Effective date. This regulation shall become effective
(insert date of publication in the FEDERAL REGISTER).

(Secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348).).

Dated: _____.



UNION CARBIDE CORPORATION.

OLD SAW MILL RIVER ROAD, TARRYTOWN, NY 10591
Research and Development
Silicones & Urethane Intermediates Division

May 19, 1983

Mr. Julius Smith
U.S. Dept. of Health & Human Services
Petitions Control Branch, HFF-334
Division of Food and Color Additives
Bureau of Foods
Food & Drug Administration
Washington, D.C. 20204

Re: Food Additive Petition No. 8B3394

Dear Mr. Smith:

Responsive to your correspondence of 5 May, 1983 regarding the above referenced petition, I have examined the draft documents included therewith and find no exception to either the content or the language.

Your continued expeditious handling of this entire petition process is appreciated.

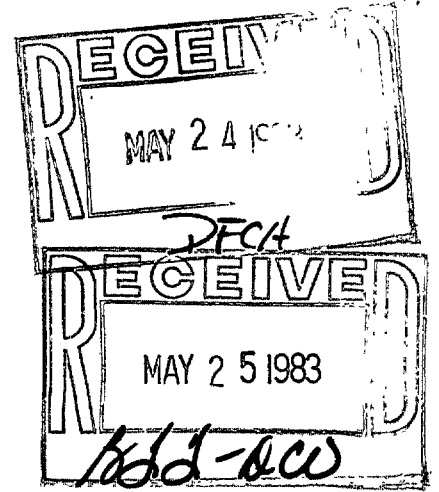
Sincerely,

A handwritten signature in dark ink, appearing to be "R.S. Pender", written over the word "Sincerely".

R.S. Pender

RSP:m1

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000218.001



DEPARTMENT OF HEALTH & HUMAN SERVICES

Memorandum

Date . **AUG 8 1983**

From Associate Director for Compliance
Bureau of Foods, (HFF-300)

Subject Amendment to Part 177 Indirect Food Additives: Polymers
Food Additive Petition No. 8B3394 - ACTION

To: Director, Bureau of Foods (HFF-1) *[Signature]*

OBJECTIVE

This food additive regulation is for the signature of the Director of the Bureau of Foods, HFF-1, because it does not involve novel or controversial issues, and does not involve any question about the applicability of the Delaney Clause. This regulation is for publication in the Federal Register.

FACTS

The attached order (Tab A) would amend Part 177 (21 CFR 177) of the food additive regulations to provide for the safe use of fluorine treated polyethylene as a food contact surface.

DISCUSSION

The subject resin is a surface modified polyethylene that is produced by treating polyethylene with a mixture of fluorine and nitrogen gases. This treatment results in a chemical alteration of the surface of the polymer i.e., it creates a modified, integrally bound surface layer.

The Division of Chemistry and Physics concludes that the additive is adequately identified in the order. The Division further states that if all food contact polyolefin is fluorinated by the proposed process, then the concentration of fluoride in the daily diet would be 0.23 ppm which corresponds to an estimated daily intake (EDI) of 0.69 mg/day based on a total food consumption of 3000 g/day. There is no CAS Registry number for polyethylene modified by surface fluorination.

The Division of Toxicology concludes that the additive is safe under the condition as prescribed in the order. This conclusion is based on the estimated daily intake of 0.69 mg/day for fluoride ion and on chemical data which indicate that fluorination is a surface phenomenon and the organic migrants to food are the usual low molecular weight polyolefin extractives as characterized for the polyolefins already regulated.

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DEPARTMENT OF HEALTH AND HUMAN SERVICES

AUG 8 1983

BEST ORIGINAL COPY

Associate Director for Compliance
Bureau of Foods, (HFF-300)

Amendment to Part 177 Indirect Food Additives: Polymers
Food Additive Petition No. 8B3394 - ACTION

To: Director, Bureau of Foods (HFF-1)

~~Assoc. Dir. Bureau of Foods~~
~~for HFF-1~~
for HFF-1

OBJECTIVE

This food additive regulation is for the signature of the Director of the Bureau of Foods, HFF-1, because it does not involve novel or controversial issues, and does not involve any question about the applicability of the Delaney Clause. This regulation is for publication in the Federal Register.

FACTS

The attached order (Tab A) would amend Part 177 (21 CFR 177) of the food additive regulations to provide for the safe use of fluorine treated polyethylene as a food contact surface.

DISCUSSION

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The Division of Chemistry and Physics concludes that the additive is adequately identified in the order. The Division further states that if all food contact polyolefin is fluorinated by the proposed process, then the concentration of fluoride in the daily diet would be 0.23 ppm which corresponds to an estimated daily intake (EDI) of 0.69 mg/day based on a total food consumption of 3000 g/day. There is no CAS Registry number for polyethylene modified by surface fluorination.

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(b) (5)

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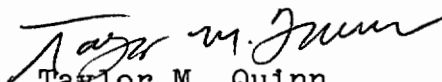
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The Environmental Impact Section has reviewed the environmental impact of this action (Tab C) and has concluded that the regulation of this additive will not significantly affect the quality of the human environment and that no environmental impact statement is necessary. The finding of no significant impact and supporting data are attached as (Tab C) for display at the Dockets Management Branch.

The Division of Food and Color Additives concludes that Regulatory Flexibility and Regulatory Impact analyses are not necessary because the proposed action is exempt from the Regulatory Flexibility Act and Executive Order 12291. The Division also concludes that this regulation falls within the scope of the delegation of authority for signature by the Director or Deputy Director of the Bureau of Foods. This regulation represents a routine amendment to the regulations.

RECOMMENDATION

We recommend that the enclosed order be signed and published in the Federal Register.


Taylor M. Quinn

Enclosures

Tab A - Document
Tab B - Filing Notice
Tab C - Environmental Impact Analysis Report and Finding
of no Significant Impact

DECISION

Approved



Disapproved

Date

8/18/83.

5-13-83

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83-392

ROUTING OF FEDERAL REGISTER DOCUMENT

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1753

Indirect Food Additives; Polymers

FAP8B33 94

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J. Smith

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ACTION REQUIRED ON DOCUMENT

(b) (5)

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DEPARTMENT OF HEALTH AND HUMAN SERVICES
FOOD AND DRUG ADMINISTRATION

21 CFR PART 177

[DOCKET NO. 83F-0049]

INDIRECT FOOD ADDITIVES; POLYMERS

AGENCY: Food and Drug Administration.

ACTION: Final rule.

SUMMARY: The Food and Drug Administration (FDA) is amending the food additive regulations to provide for safe use of fluorine-treated polyethylene as a food-contact surface. This action responds to a petition filed by the Union Carbide Corp.

DATES: Effective (insert date of publication in the FEDERAL REGISTER); objection by (insert date 30 days after date of publication in the FEDERAL REGISTER).

ADDRESS: Written objections to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT:

Julius Smith,
Bureau of Foods (HFF-334),
Food and Drug Administration,
200 C St. SW.,
Washington, DC 20204,
202-472-5690.

SUPPLEMENTARY INFORMATION: In a notice published in the FEDERAL REGISTER of March 29, 1983 (48 FR 13098), FDA announced that a petition (FAP 8B3394) had been filed by the Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that the food additive regulations be amended to provide for safe use of fluorine-treated polyethylene as a component of food-contact surfaces.

FDA has evaluated the data in the petition and concludes that the proposed food additive use is safe and that the regulations should be amended as set forth below.

In accordance with § 171.1(h) (21 CFR 171.1(h)), the petition and the documents that FDA considered and relied upon in reaching its decision to approve the petition are available for inspection at the Bureau of Foods (address above) by appointment with the information contact person listed above. As provided in § 171.1(h)(2), the agency will delete from the documents any materials that are not available for public disclosure before making the documents available for inspection.

The agency has considered the potential environmental effects of this action and has concluded that the action will not have a significant impact on the human environment and that an environmental impact statement is not required. The agency's finding of no significant impact and the evidence supporting that finding may be seen in the Dockets Management Branch (address above), between 9 a.m. and 4 p.m., Monday through Friday.

List of Subjects in 21 CFR Part 177

Food additives; Polymeric food packaging.

Therefore, under the Federal Food, Drug, and Cosmetic Act (secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348)) and under authority delegated to the Commissioner of Food and Drugs (21 CFR 5.10) and redelegated to the Bureau of Foods (21 CFR 5.61), Part 177 is amended in Subpart B by adding new § 177.1615, to read as follows:

PART 177--INDIRECT FOOD ADDITIVES: POLYMERS

§ 177.1615 Polyethylene, fluorinated.

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food-contact articles in accordance with the following prescribed conditions:

(a) Fluorinated polyethylene food-contact articles are produced by modifying the surface of polyethylene articles through action of fluorine gas in combination with gaseous nitrogen as an inert diluent. Such modification affects only the surface of the polymer, leaving the interior unchanged.

Fluorinated polyethylene articles are manufactured from basic resins containing not less than 85 weight-percent of polymer units derived from ethylene and identified in § 177.1520(a)(2) and (3)(i).

(b) Fluorinated polyethylene articles conform to the specifications and use limitations of § 177.1520(c), items 2.1 and 3.1.

(c) The finished food-contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of § 176.170(c) of this chapter, yields fluoride ion not to exceed 5 parts per million calculated on the basis of the volume of food held by the food-contact article.

Any person who will be adversely affected by the foregoing regulation may at any time on or before (insert date 30 days after date of publication in the FEDERAL REGISTER) submit to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857, written objections thereto and may make a written request for a public hearing on the stated objections. Each objection shall be separately numbered and each numbered objection shall specify with particularity the provision of the regulation to which objection is made. Each numbered objection on which a hearing is requested shall specifically so state; failure to request a hearing for any particular objection shall constitute a waiver of the right to a hearing on that objection. Each numbered objection for which a hearing is requested shall include a

detailed description and analysis of the specific factual information intended to be presented in support of the objection in the event that a hearing is held; failure to include such a description and analysis for any particular objection shall constitute a waiver of the right to a hearing on the objection. Three copies of all documents shall be submitted and shall be identified with the docket number found in brackets in the heading of this regulation. Received objections may be seen in the office above between 9 a.m. and 4 p.m., Monday through Friday.

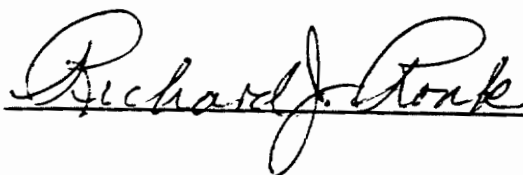
Effective date. This regulation shall become effective
(insert date of publication in the FEDERAL REGISTER).

(Secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348).).

Dated: _____

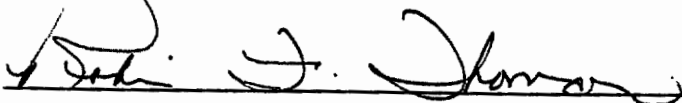
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AUG 18 1983



Richard J. Ronk
Acting Director,
Bureau of Foods

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FEDERAL REGISTER
AUGUST 29, 1983
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& 39058

FAP 3B3394
J. SMITH

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as a food-contact surface. This action responds to a petition filed by the Union Carbide Corp.

DATES: Effective August 29, 1983; objection by September 28, 1983.

ADDRESS: Written objections to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT: Julius Smith, Bureau of Foods (HFF-334), Food and Drug Administration, 200 C St. SW., Washington, DC 20204, 202-472-5690.

SUPPLEMENTARY INFORMATION: In a notice published in the Federal Register of March 29, 1983 (48 FR 13098), FDA announced that a petition (FAP 8B3394) had been filed by the Union Carbide Corp., Old Saw Mill River Rd., Tarrytown, NY 10591, proposing that the food additive regulations be amended to provide for safe use of fluorine-treated polyethylene as a component of food-contact surfaces.

FDA has evaluated the data in the petition and concludes that the proposed food additive use is safe and that the regulations should be amended as set forth below.

In accordance with § 171.1(h) (21 CFR 171.1(h)), the petition and the documents that FDA considered and relied upon in reaching its decision to approve the petition are available for inspection at the Bureau of Foods (address above) by appointment with the information contact person listed above. As provided in § 171.1(h)(2), the agency will delete from the documents any materials that are not available for public disclosure before making the documents available for inspection.

The agency has considered the potential environmental effects of this action and has concluded that the action will not have a significant impact on the human environment and that an environmental impact statement is not required. The agency's finding of no significant impact and the evidence supporting that finding may be seen in the Dockets Management Branch (address above), between 9 a.m. and 4 p.m., Monday through Friday.

List of Subjects in 21 CFR Part 177

Food additives, Polymeric food packaging.

Therefore, under the Federal Food, Drug, and Cosmetic Act (secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348)) and under authority delegated to the Commissioner of Food and Drugs (21 CFR 5.10) and redelegated to the Bureau of Foods (21 CFR 5.61), Part 177 is amended in Subpart B by

adding new § 177.1615, to read as follows:

PART 177—INDIRECT FOOD ADDITIVES: POLYMERS

§ 177.1615 Polyethylene, fluorinated.

Fluorinated polyethylene, identified in paragraph (a) of this section, may be safely used as food-contact articles in accordance with the following prescribed conditions:

(a) Fluorinated polyethylene food-contact articles are produced by modifying the surface of polyethylene articles through action of fluorine gas in combination with gaseous nitrogen as an inert diluent. Such modification affects only the surface of the polymer, leaving the interior unchanged. Fluorinated polyethylene articles are manufactured from basic resins containing not less than 85 weight-percent of polymer units derived from ethylene and identified in § 177.1520 (a)(2) and (3)(i).

(b) Fluorinated polyethylene articles conform to the specifications and use limitations of § 177.1520(c), items 2.1 and 3.1.

(c) The finished food-contact article, when extracted with the solvent or solvents characterizing the type of food and under conditions of time and temperature characterizing the conditions of its intended use as determined from tables 1 and 2 of § 176.170(c) of this chapter, yields fluoride ion not to exceed 5 parts per million calculated on the basis of the volume of food held by the food-contact article.

Any person who will be adversely affected by the foregoing regulation may at any time on or before September 28, 1983 submit to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm 4-62, 5600 Fishers Lane, Rockville, MD 20857, written objections thereto and may make a written request for a public hearing on the stated objections. Each objection shall be separately numbered and each numbered objection shall specify with particularity the provision of the regulation to which objection is made. Each numbered objection on which a hearing is requested shall specifically so state; failure to request a hearing for any particular objection shall constitute a waiver of the right to a hearing on that objection. Each numbered objection for which a hearing is requested shall include a detailed description and analysis of the specific factual information intended to be presented in support of the objection in the event that a hearing is held; failure to include such

DEPARTMENT OF HEALTH AND HUMAN SERVICES

Food and Drug Administration

21 CFR Part 177

[Docket No. 83F-0049]

Indirect Food Additives; Polymers

AGENCY: Food and Drug Administration.

ACTION: Final rule.

SUMMARY: The Food and Drug Administration (FDA) is amending the food additive regulations to provide for safe use of fluorine-treated polyethylene

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a description and analysis for any particular objection shall constitute a waiver of the right to a hearing on the objection. Three copies of all documents shall be submitted and shall be identified with the docket number found in brackets in the heading of this regulation. Received objections may be seen in the office above between 9 a.m. and 4 p.m., Monday through Friday.

Effective date. This regulation shall become effective August 29, 1983.

(Secs. 201(s), 409, 72 Stat. 1784-1788 as amended (21 U.S.C. 321(s), 348))

Dated: August 18, 1983.

Richard J. Ronk,
Acting Director, Bureau of Foods.

[FR Doc. 83-23554 Filed 8-28-83; 8:45 am]

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