CH-1 REV. 7-80

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
WILMINGTON, DELAWARE 19898

CHEMICALS AND PIGMENTS DEPARTMENT

Specialty Chemical Products Division
Specialty Chemical Technical Section
Technical Laboratory

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August 16, 1984

Mr. Marvin Kirkwood
Du Pont Canada, Inc.
Research Center
P. O. Box 5000
Front Road
Kingston, Ontario
Canada K7L 5A5

Dear Marv:

Enclosed is a copy of our petition for F.D.A. approval of "Zonyl" RP (and "Zonyl" NF). Also enclosed is a copy of the Federal Registrar wherein "Zonyl" RP is described. The specific F.D.A. clearances are further detailed in the enclosed product bulletins.

As we discussed, we would appreciate your assistance in getting "Zonyl" RP approved for use on paper and paperboard in Canada. 3-M's competitive products are FC-807 and FC-809.

If I can provide additional information, please call.

Sincerely,

Louis B. Fournier

Louis B. Fournier
(609) 540-2796

LBF:fgb
Enclosures
1545B

§ 121.2526 Components of paper and paperboard in contact with aqueous and fatty foods.

Substances identified in this section may be safely used as components of the uncoated or coated food-contact surface of paper and paperboard intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding aqueous and fatty foods, subject to the provisions of this section. Components of paper and paperboard in contact with dry food of the type identified under type VIII of table 1 in paragraph (c) of this section are subject to the provisions of § 121.2571.

(a) Substances identified in subparagraphs (1) through (5) of this paragraph may be used as components of the food-contact surface of paper and paperboard. Paper and paperboard products shall be exempted from compliance with the extractives limitations prescribed in paragraph (c) of this section: *Provided*, That the components of the food-contact surface consist entirely of one or more of the substances identified in this paragraph: *And provided further*, That if the paper or paperboard when extracted under the conditions prescribed in paragraph (c) of this section exceeds the limitations on extractives contained in paragraph (c) of this section, information shall be available from manufacturing records from which it is possible to determine that only substances identified in this paragraph (a) are present in the food-contact surface of such paper or paperboard.

(1) Substances generally recognized as safe in food.

(2) Substances generally recognized as safe for their intended use in paper and paperboard products used in food packaging.

(3) Substances used in accordance with a prior sanction or approval.

(4) Substances that by regulation in this Part 121 may be safely used without extractives limitations as components of the uncoated or coated food-contact surface of paper and paperboard in contact with aqueous or fatty food, subject to the provisions of such regulation.

(5) Substances identified in this subparagraph, as follows:

List of substances	Limitations
Acetyl peroxide	For use only as polymerization catalyst.
Acrylamide-β-methacryloxyethyltrimethylammonium methyl sulfate copolymer resins containing not more than 5 molar percent of dimethacryloxyethyltrimethylammonium methyl sulfate and containing less than 0.2% of residual acrylamide monomer.	For use only as a retention aid and flocculant employed prior to the sheet-forming operation in the manufacture of paper and paperboard.
tert-Alkyl(C$_{12}$–C$_{16}$)mercaptans	For use only as polymerization-control agent.
Aluminum acetate	
Ammonium persulfate	
Ammonium thiosulfate	
Azo-bis-isobutyronitrile	For use only as polymerization catalyst.
Benzoyl peroxide	Do.
N,N-Bis(2-hydroxyethyl)alkyl (C$_{12}$–C$_{18}$)amide.	For use only as an adjuvant to control pulp absorbency and pitch content in the manufacture of paper and paperboard prior to the sheet-forming operation.
tert-Butyl hydroperoxide	For use only as polymerization catalyst.
tert-Butyl peroxide	Do.
Carrageenan and salts of carrageenan as described in §§ 121.1060 and 121.1061.	
Castor oil, hydrogenated	
Castor oil, sulfated, ammonium, potassium, or sodium salt.	
Cellulose, regenerated	
Chloroacetamide	For use only as polymerization-control agent.
Cobaltous acetate	For use only as polymerization catalyst.
Cumene hydroperoxide	Do.
Cyanoguanidine	For use only: 1. As a modifier for amino resins. 2. As a fluidizing agent in starch and protein coatings for paper paper and paperboard.
Dialdehyde guar gum	For use only as a wet-strength agent employed prior to the sheet-forming operation in the manufacture of paper and paperboard and used at a level not to exceed 1% by weight of the finished dry paper and paperboard fibers.
Dialdehyde locust bean gum	Do.
2,5-Di-*tert*-butyl hydroquinone	For use only as an antioxidant for fatty based coating adjuvants provided it is used at a level not to exceed 0.005% by weight of coating solids.

Amendment published in Federal Register:
★ August 29, 1967; 32 F.R. 12474

Remove old page 28.1 and insert this new page in your reprint.

"Zonyl" RP
TLF 2724

List of substances	Limitations
Diethanolamine	For use only as an adjuvant to control pulp absorbency and pitch content in the manufacture of paper and paperboard prior to the sheet-forming operation.
★ Diethanolamine salts of mono- and bis(1H,1H,2H,2H-perfluoroalkyl) phosphates where the alkyl group is even-numbered in the range C_8–C_{18} and the salts have a fluorine content of 52.4% to 54.4% as determined on a solids basis.	For use only as an oil and water repellent at a level not to exceed 0.17 pound (0.09 pound of fluorine) per 1,000 square feet of treated paper or paperboard, as determined by analysis for total fluorine in the treated paper or paperboard without correction for any fluorine which might be present in the untreated paper or paperboard, when such paper or paperboard is used in contact with nonalcoholic foods under the conditions of use described in paragraph (c) of this section, table 2, conditions of use (E), (F) and (G). ★
Diethylenetriamine	For use only as a modifier for amino resins.
N,N-Diisopropanolamide of tallow fatty acids.	For use only as an adjuvant to control pulp absorbency and pitch content in the manufacture of paper and paperboard prior to the sheet-forming operation.
N,N'-Dioleoylethylenediamine	
Diphenylamine	For use only as an antioxidant for fatty based coating adjuvants provided it is used at a level not to exceed 0.005% by weight of coating solids.
Dipropylene glycol	
N,N'-Distearoylethylenediamine.	
Fatty acids derived from animal and vegetable fats and oils and salts of such acids, single or mixed, as follows: Aluminum. Ammonium. Calcium. Magnesium. Potassium. Sodium. Zinc.	
Ferric chloride	
Ferrous ammonium sulfate	
Fish oil, hydrogenated	

List of substances	Limitations
Fish oil, hydrogenated, potassium salt.	
Ferrocyanide and salts of ferrocyanide as described in §§ 121.1028 and 121.1029.	
Glyceryl lactostearate	
Glyceryl mono-12-hydroxystearate.	
Glyceryl monoricinoleate	
Hexamethylenetetramine	For use only as polymerization cross-linking agent for protein, including casein.
Hydroquinone and the monomethyl or monoethyl ethers of hydroquinone.	For use only as an inhibitor for monomers.
Isopropyl *m*- and *p*-cresols (thymol derived).	For use only as an antioxidant for fatty based coating adjuvants provided it is used at a level not to exceed 0.005% by weight of coating solids.
Isopropyl peroxydicarbonate	For use only as polymerization catalyst.
Japan wax	
Lanolin	
Lauryl peroxide	For use only as polymerization catalyst.
~~Lauryl sulfate salts: Ammonium. Magnesium. Potassium. Sodium.~~	
Lecithin, hydroxylated	
Lignin sulfonate and its calcium, potassium, and sodium salts.	
Methyl naphthalene sulfonic acid-formaldehyde condensate, sodium salt.	For use only as an adjuvant to control pulp absorbency and pitch content in the manufacture of paper and paperboard prior to the sheet-forming operation.
Mineral oil, white	
Monoglyceride citrate	
Mustardseed oil, sulfated, ammonium, potassium, or sodium salt.	
Naphthalene sulfonic acid-formaldehyde condensate, sodium salt.	For use only as an adjuvant to control pulp absorbency and pitch content in the manufacture of paper and paperboard prior to the sheet-forming operation.
Nitrocellulose, 10.9–12.2% nitrogen.	
Oleic acid, sulfated, ammonium, potassium, or sodium salt.	
N-Oleyl-*N'*-stearoylethylenediamine.	
Oxystearin	
Paraformaldehyde	For use only as setting agent for protein.
Petrolatum	Complying with § 121.2585.
Petroleum asphalt, steam and vacuum refined to meet the following specifications: Softening point 140° F.–240° F., as determined by ASTM Method D-36; penetration at 77° F., not to exceed 10.5 mm., as determined by ASTM Method D-5, and maximum weight loss not	For use only as a component of internal sizing of paper and paperboard [illegible] use in contact only with raw [illegible] [illegible] and dry [illegible]

C+D

"ZONYL" RP PAPER FLUORIDIZER
INDIRECT ADDITIVE FOR FOOD IN CONTACT WITH PAPER AND PAPERBOARD

A. Identity and Composition

1-a. Common Name

"Zonyl" RP does not have a common name.

1-b. Chemical Name

The chemical name of the product is mono and bis (1H, 1H, 2H, 2H perfluoroalkyl phosphates, diethanolammonium salts.

1-c. Trade Name

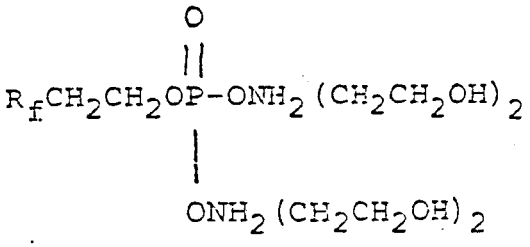
The trade name is "Zonyl" RP, a paper fluoridizer marketed by the Du Pont Company under the registered trademark "Zonyl".

2-a. Empirical Formula

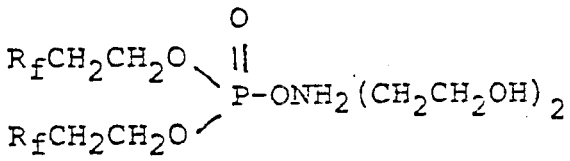
"Zonyl" RP is a mixture, the active portion of which comprises the diethanolamine salts of an equimolar mixture of mono and bis (perfluoroalkyl) phosphates. The empirical formula for the mono perfluoroalkyl phosphate is $C_{18}F_{17}H_{28}N_2O_8P$. The empirical formula for the bis perfluoroalkyl phosphate is $C_{24}F_{34}H_{20}NO_6P$.

2-b. Structural Formula

The structural formula for the mono (perfluoroalkyl) phosphate is,



and for the bis (perfluoroalkyl) phosphate is,



Where R_f = C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$, $C_{12}F_{25}$, $C_{14}F_{29}$ and $C_{16}F_{33}$

Chemically these compounds are named mono (1H, 1H, 2H, 2H perfluoroalkyl) phosphate, diethanolammonium salt and bis (1H, 1H, 2H, 2H perfluoroalkyl) phosphate, diethanolammonium salt.

2-c. Molecular Weight

The average molecular weight of the mono perfluoroalkyl phosphate is about 754 and of the bis perfluoroalkyl phosphate is about 1095.

The mixture of salts is diluted to a 33% solution (weight percent) with 10% "Freon" 113 (CCl_2F-CF_2Cl), 20% isopropanol $[(CH_3)_2CHOH]$ and water.

The solvents do not contribute to the utility of the product; they are used solely to permit the marketing of "Zonyl" RP as a reasonably concentrated solution. During the application of "Zonyl" RP to paper, the solvents are removed by drying.

3. Composition of Food Contact Surface

a. Basic Material

The food contact surface is paper or paperboard containing up to 0.14 lbs. of mixed mono and bis perfluoroalkyl phosphate diethanolammonium salts per 1,000 square feet of exposed surface.

b. Adjuvants

The paper or paperboard may contain in addition water repellents, cationic resin retention aids, pigments, clays and binding agents. All adjuvants are used in accordance with good commercial practice and are selected from those generally recognized as safe, the subject of a prior sanction or approval or the subject of a regulation in Subpart F of Part 121-Food Additives.

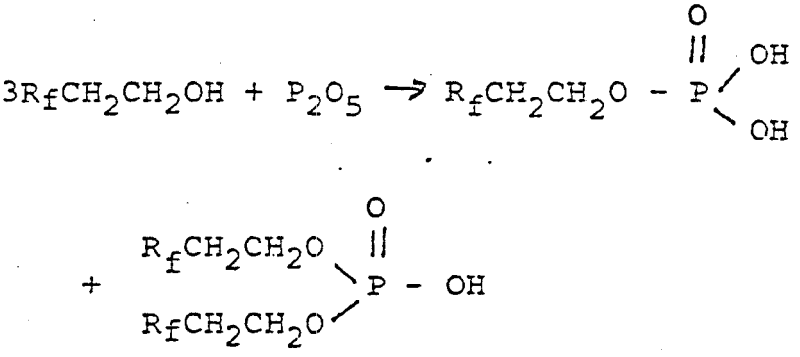
c. Impurities

There are no impurities such as heavy metals, monomers, catalyst residues, etc. introduced by application of the "Zonyl" RP to paperboard.

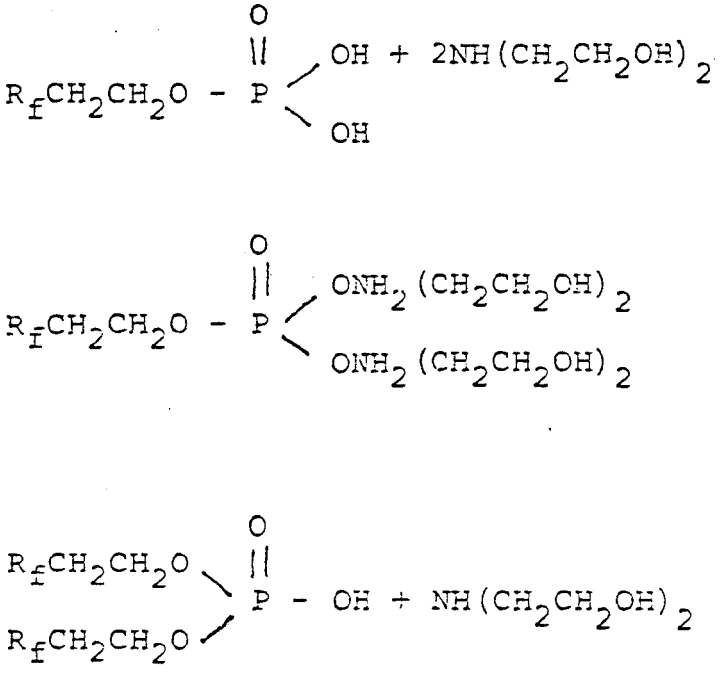
4. Manufacturing Process

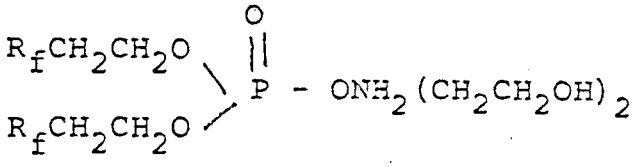
"Zonyl" RP is made by reacting 3 moles of 1H, 1H, 2H, 2H perfluoroalkyl alcohol with 1 mole of phosphoric anhydride. The mixture of acid phosphates produced is neutralized with diethanolamine.

The reaction to make the acid phosphates is:



The neutralization of the acid phosphates with diethanolamine is as follows:





The basic intermediate in the process is the 1H, 1H, 2H, 2H perfluoroalkyl alcohol. This intermediate is controlled for composition by vapor phase chromatography and molecular weight range by hydroxyl number. The perfluoroalkyl alcohol contains a minimum of 95% of the alcohol, a maximum of 2.5% perfluoroalkyl iodide and of 2.5% perfluoroalkanes (C_nF_{2n+2}). The hydroxyl number is 117 ± 3 corresponding to an average molecular weight of 478 and an average composition of $C_8F_{17}(CH_2)_2OH$. =464 calc.

The control of molecular weight in the phosphation step is by reaction to a specified acid number range, 109 ± 3. The fluorine content of the reaction mass is determined by combustion of a sample by the Wickbold Torch procedure (Orchem Method 9-8-1A) followed by determination of the fluoride in the torch effluent by a method (Orchem 2-10-10) based on the use of a fluoride ion electrode. In this analytical method, the potential of the unknown solution is determined, an addition of a known concentration of fluoride ion made and the potential redetermined,

after which the fluoride ion concentration in the unknown is calculated by means of the Nernst Equation. This method replaces the use of the thorium nitrate titration procedure (Orchem Method 2-74-1) used in connection with Food Additive Petition No. 5B1747. The fluorine content of the un-neutralized perfluoroalkyl phosphate must be within the limits 62.2 - 64.6% for acceptable material. Copies of the Methods 9-8-1A (Wickbold Torch procedure), 2-10-10 (fluoride ion electrode) and 2-74-1 (thorium nitrate titration procedure) are attached to Section E - Methodology.

The neutralization step is carefully controlled by adding 1.03 moles of diethanolamine per mole equivalent of the perfluoroalkyl phosphate.

The fluorine content in the neutralized solids is calculated from the fluorine content of the perfluoroalkyl phosphate and the weight of diethanolamine used in the neutralization step. The calculated fluorine content is checked against the actual fluorine analysis of a laboratory neutralized plant production sample of the perfluoroalkyl phosphate. Acceptable "Zonyl" RP has a fluorine content of 53.4 $\pm$ 1.0% based on the neutralized solids.

The neutralized reaction mass is dissolved in a mixture of 1,1,2 trichloro-1,2,2 trifluoroethane, isopropanol and water while adjusting the perfluoroalkyl phosphate diethanolamine salt content to a minimum of 33%. The active ingredient content is determined by evaporation of solvent from a weighed sample followed by drying in a vacuum oven at 120°C. for 2 hours at 20 mm. pressure as described in Orchem Method 90-9-4-1A. A copy is attached to Section E - Methodology.

The effectiveness of the "Zonyl" RP as an oil repellent is checked by application of 0.30% product on the weight of paper and observing for holdout of peanut oil under standard conditions. A solution of 0.228 gms. of "Zonyl" RP per 100 ml. of water is prepared. A weighed strip of unbleached kraft paper is immersed in the test solution for 15 seconds at room temperature. The strip is squeezed to remove excess solution and obtain a wet pickup of solution of 130 - 135%. The treated strip is dried on a drum dryer at 180°F., then conditioned 4 hours at 65% relative humidity and 70°F. Three drops of a dyed peanut oil are placed on the paper strip and the time required for the oil to penetrate noticeably is determined. Satisfactory production will provide an oil holdout greater than 30 minutes under these conditions.

5. Physical, Chemical and Biological Properties

Physical Properties

Appearance	Clear, light brown liquid
Odor	Alcoholic (isopropanol)
Active Ingredient	33%
Density at 77°F.	9.75 lb./gal.
Viscosity at 77°F.	10 cps.
Flash Point (Tag open cup)	106°F. (41°C.)
pH	7.5 ± 1.0
Solubility	
In water	All proportions
In polar solvents	Slight
In non-polar solvents	Negligible

Chemical Properties

1. "Zonyl" RP is stable over a wide range of pH, including strong mineral acids and alkalies.
2. "Zonyl" RP reacts with salts of alkaline earths and heavy metals to give relatively water-insoluble salts of the fluoroalkyl phosphate by double displacement.
3. Oxidative decomposition of "Zonyl" RP requires burning in an atmosphere of oxygen; the composition is stable to less vigorous oxidizing systems.
4. "Zonyl" RP is essentially neutral and is not corrosive.

Biological Properties

The use of "Zonyl" RP as an oil and grease repellent on paper and paperboard has been the subject of discussions with and a petition to the Food and Drug Administration. All available toxicity data were presented to the Food and Drug Administration during consideration of Food Additive Petition No. 5B1747. The Du Pont Company Haskell Laboratory for Toxicology and Industrial Medicine concurs that these data are pertinent and applicable for consideration of this new petition and support the safety of the uses proposed.

Presentation of a report on "Use of 'Zonyl' RP Paper Fluoridizer for Edge Treating Paper and Paperboard Containers for Bakery Products, Candy and Bacon" was made by the letter of R. H. Rea to William F. Randolph dated September 24, 1964. Discussions of this report led to agreement by FDA that the use of "Zonyl" RP in edge treating paper and paperboard containers for packaging cake mixes, bacon, and similar foods will present no food additive problem when used as described. (Ref. letter W. F. Randolph to R. H. Rea, 2-10-65). The edge treatment uses are now covered by a current regulation

and it is not planned to repeat this request as suggested in FDA Opinion Letter, April 9, 1970, Policy Statement.

Food Additive Petition No. 5B1747 initiated by the letter of D. I. Cashell to William F. Randolph, dated April 9, 1965, led to an amendment of Regulation 121.2526 (a) (5) by alphabetically inserting in the list of substances:

"Diethanolamine salts of mono and bis (1H, 1H, 2H, 2H perfluoroalkyl) phosphates where the alkyl group is even-numbered in the range C_8-C_{18} and the salts have a fluorine content of 52.4 to 54.4% as determined on a solids basis" subject to the limitations "For use only as an oil and water repellent at a level not to exceed 0.17 pound (0.09 pound of fluorine) per 1,000 square feet of treated paper or paperboard, as determined by analysis for total fluorine in the treated paper or paperboard without correction for any fluorine which might be present in the untreated paper or paperboard, when such paper or paperboard is used in contact with nonalcoholic foods under the conditions of use described in paragraph (c) of this section, table 2, conditions of use (E), (F) and (G)". While it is not spelled out in the published regulation concerning "Zonyl" RP, it is understood that the guideline in setting the maximum

concentration limit on the paper or paperboard was a maximum extractability of "Zonyl" RP solids of 0.2 ppm. at 10 ml. per square inch in tests with food simulating solvents.

6. Specifications

The product specifications for "Zonyl" RP is as follows:

(1) The product shall be a clear, dark yellow to medium amber liquid, which may contain a noticeable content of fine solids.

(2) Its specific gravity, 25/25°C., shall be 1.172 $\pm$ 0.012.

(3) Its pH, measured at 25°C., shall be 7.5 $\pm$ 1.0.

(4) Its active ingredient content shall be 34.0 $\pm$ 1.0% by weight. Determine by Orchem Method 90-9-4-1A. (Copy attached to Section E - Methodology).

(5) The deposition of 0.30% maximum of "Zonyl" RP (as received) on a waterleaf unbleached kraft paper by an immersion squeeze technique shall repel drops of peanut oil for at least 30 minutes.

B. Usage

The use of "Zonyl" RP in oil, grease and water repellent finishes on paper and paperboard for the packaging of fatty and aqueous foods is now regulated subject to Conditions (E), (F), and (G) of Table 2 of Regulation 121.2526.

The utility of the perfluoroalkyl phosphate diethanolamine salt as an oil and grease repellent finish on paperboard is demonstrated commercially by the large scale use in cartons for packaging various foods such as chocolate candy, pecans, peanuts, margarine, bacon, pet foods and bakery products such as Danish pastry and doughnuts.

Current practices in food packaging and distribution require the filling of packages with hot foods in many instances (Conditions C and D). For example, some types of pet food may be packaged hot as well as at room temperature. The food will be molded as it goes through a conveyer-type oven. Before leaving the oven, it is sprayed with animal fat which can be at a temperature between 120° and 160°F. The food itself may be even hotter. It is dropped into a collecting hopper and fed into the packaging machine. Older plants may utilize a storage bin, in which case the food cools. Newer plants are more stream-lined, have faster loading machines, and the product is packaged hot.

Other foods that may be packaged hot include cakes, cookies, crackers, doughnuts, potato chips and snack foods. In all cases, the elevated temperature at the time of packaging will drop rapdily and reach ambient temperatures, usually in a short time and certainly within a very few hours.

There is the rapidly growing distribution of hot food by "carry out" from the place of preparation followed by eating at some other location. Examples are fried chicken and french fried potatoes packaged directly from the fryer. Other examples are pizza, hamburgers and fried seafood. The temperature of the food in the package will drop to warm, c.a. 110°F., within an hour and it is usually consumed within this time.

Use of "Zonyl" RP treated paper and paperboard under Conditions (C) and (D) of Table 2 of Regulation 121.2526 is not presently permitted and this petition is intended to extend the present coverage--Conditions of Use (E), (F), and (G)--to include Conditions of Use (C) and (D).

C. Intended Technical Effect

The purpose of the perfluoroalkyl phosphate finish on the paperboard carton is to eliminate wicking of oil or grease from the packaged food into the cardboard with advantages of good package appearance, no loss of oil or fat from the food, and no danger of transfer of oil or fat from the greasy surface of a package to apparel of people or to upholstery of automobiles during handling and transport.

Several systems can be used for application of "Zonyl" RP to paper or paperboard to achieve oil and grease repellency. These include surface application by dipping, roll transfer, or spraying, by internal application before forming the sheet or by application in conjunction with some other coating system.

Surface treatments can be made on or off the paper machine. Convenient locations on the machine are in the press section (as at a feltless smoothing press), at the size tub, size press, coater or calender. One-sided or two-sided treatments can be made, but one-sided is often sufficient, this being determined by the end use of the paper or paperboard. In

off machine treatments, as in a converting operation, applications are usually made by a roller coater operation.

The amount of "Zonyl" RP applied by these surface techniques in general varies from 0.04 to 0.14 pounds on a solids basis for 1,000 square feet of paperboard and depends on exposure conditions and the degree of resistance to oil or grease penetration needed for the end use. For example, from 0.1 to 0.14 pounds of solids per 1,000 square feet of paperboard is needed to hold out the oils and greases from hot foods such as fried chicken, french fried potatoes, hamburgers, and pizza. Similar concentrations are needed on paperboard used in the packaging of margarine, bacon and bakery products such as doughnuts and "brown and serve" rolls. Lower concentrations in the range 0.04 to 0.1 pound of solids per 1,000 square feet will provide satisfactory hold out of grease and oil in the packaging of cookies, pet foods, chocolate candy, peanuts and pecans. The cookies and pet foods may be packaged hot as well as at room temperature.

Internal application of "Zonyl" RP requires the use of a cationic retention aid which fixes the "Zonyl" RP to the individual fibers prior to sheet formation. The cationic fixing agent and the "Zonyl" RP are mixed with the paper pulp;

the oil and grease repellent paperboard is formed from the pulp. The amount of "Zonyl" RP solids will vary from about 0.15 - 0.35% or an upper limit of about 0.14 pounds per 1,000 square feet of paperboard to be used under hot filling conditions.

As a result of Food Additive Petition 5B1747, a regulation was issued establishing an upper limit of 0.17 pounds "Zonyl" RP solids per 1,000 square feet of treated paper and paperboard. However, use experience has demonstrated that an upper limit of 0.14 pounds per 1,000 square feet of treated paper or paperboard is all that is necessary, not only for Use Conditions (C) and (D) but (E), (F), and (G) as well. As a result, the amendment as proposed on Page 25 hereof reduces the upper limit to 0.14 pounds per 1,000 square feet of treated paper or paperboard and requests coverage for Conditions (C), (D), (E), (F), and (G) at this lower rate.

D. Quantity of the Indirect Additive in Food

1. Extraction Data

Possible uses for "Zonyl" RP treated paper and paperboard were reviewed in light of Tables 1 and 2 of Indirect Food Additive Regulation 121.2526. It was concluded that all types of raw and processed foods, with the exception of alcoholic beverages and dry solids as characterized by VI, and VIII of Table 1, could be expected to come in contact with "Zonyl" RP treated board.

The following conditions of use are currently covered under Regulation 121.2526:

E - Room temperature filled and stored (no thermal treatment in the container)

F - Refrigerated storage (no thermal treatment in the container)

G - Frozen storage (no thermal treatment in the container)

This new petition has particular interest in the following additional conditions of use:

C - Hot filled or pasteurized above 150°F.

D - Hot filled or pasteurized below 150°F.

To cover the various types of food expected to be encountered under conditions of use C and D, extraction

tests were run with water and heptane at times and temperatures detailed below. Tests were included under condition of use E, room temperature filled and stored, to provide a base for comparison as the severity of the extraction tests is increased to meet requirements of the hot filling conditions of use C and D. Extraction tests were also run as prescribed for the more demanding condition of use B to provide data for exposures of increased severity compared with those required for conditions of use C and D. The tests were made with paperboard treated to contain concentrations of "Zonyl" RP solids ranging from 0.11 to 0.17 lbs. for 1,000 square feet.

Extraction Conditions

Use Condition	Extractant	Time	Temperature
B	Water	30 min.	212°F.
C	Water	50 min.	Fill boiling - cool to 100°F.
D Extended	Water	4 hrs.	150°F.
D	Water	2 hrs.	150°F.
E	Water	24 hrs.	120°F.

Use Condition	Extractant	Time	Temperature
B (C Extended)	Heptane	30 min.	120°F.
C	Heptane	15 min.	120°F.
D Extended	Heptane	1 hr.	100°F.
D	Heptane	30 min.	100°F.
E	Heptane	30 min.	70°F.

The extractions were run in the extraction cell assembly devised for ASTM Tentative Method F-34-63T for Exposing Flexible Barrier Materials to Liquids for Extraction (described in C. M. Rosser's article in Modern Packaging, December, 1963, pp. 131-136).

The extractions were carried out on sections of paperboard taken from strips treated with "Zonyl" RP by a surface application in the laboratory. The paperboard used was a solid bleached, slack-sized board having a basis weight of 150 lbs. "Zonyl" RP was applied at levels of 0.17 and 0.14 and 0.11 pounds of solids for 1,000 square feet. The application levels were checked by fluorine analysis. The applications were made on a micro padder using the following formulations:

3.0 - 3.75% "Zonyl" RP
20.0% isopropanol
77.0 - 76.25% deionized water

Wax coated, unbleached kraft paper was used as a backing. In the application, the lower roll of the padder rotated in the application bath and carried the liquor to one side of the board at the nip. Treated samples were dried at 190°F. on a drum dryer and calendered at 375 lb. per linear inch, three times per sample, using a laboratory Fourdrinier paper machine.

In the extraction cell assemblies, two sheets of the paperboard were exposed to the extracting liquid; the "Zonyl" RP treated side was in direct contact with the liquid. Extractions were made of treated and of untreated board. Upon completion of the extraction, the liquid was poured from the cell and analyzed for total fluorine. The fluorine assay for extractions from "Zonyl" RP treated sheets, adjusted by the fluorine assay of extractions from untreated sheets, pin points the amount of "Zonyl" RP extracted. The analyses were carried out, after removal of solvent by evaporation, by combustion of the residue by the Wickbold Torch procedure (Orchem Method 9-8-1A).

followed by determination of the fluoride in the torch effluent by a Fluoride Ion Activity Method (Orchem Method 2-10-6). Method 9-8-1A is an updated version with minor revisions of Method 9-8-1 (Wickbold Torch procedure) used in Food Additive Petition No. 5B1747.

The Fluoride Ion Activity Method was used instead of the spectrophotometric procedure (Orchem Method 6-11-34) employed in Food Additive Petition No. 5B1747. The Fluoride Ion Activity Method is based on the latest technology, is more convenient and equally as accurate as the spectrophotometric method for determining low concentrations of fluorine. Copies of the Wickbold Torch procedure (Orchem Method 9-8-1) and the spectrophotometric method (Orchem Method 6-11-34) were provided to the Food and Drug Administration by the letter of J. H. James to Willard G. Orr, dated February 16, 1967, and relating to Food Additive Petition No. 5B1747. Information and data for verification of the validity of Orchem Method 9-8-1 and Orchem Method 6-11-34 was supplied to FDA by the letters of John H. James to Willard G. Orr dated February 27, 1967 and March 23, 1967, and relating to Food Additive Petition No. 5B1747. Copies of Orchem Method 9-8-1A

(Wickbold Torch procedure), 6-11-34 (spectrophotometric procedure) and 2-10-6 (Fluoride Ion Activity Method) are attached to Section E - Methodology.

The extraction tests are set forth in attached Exhibits A and B. In these exhibits, results for fluorine and "Zonyl" RP solids were calculated to give the ppm. which would be found at a ratio of extractant to treated surface of 10 milliters per square inch. Calculations were made as follows:

$$\left.\begin{array}{l}\text{ppm Fluorine}\\ \text{extracted at 10 ml.}\\ \text{extractant per}\\ \text{square inch}\end{array}\right) = \frac{\left\{\begin{array}{c}\text{gms. extractant}\\ \text{charged}\end{array}\right\} \times \left\{\begin{array}{c}\text{ppm F in extract}\\ \text{minus}\\ \text{ppm F in blank}\end{array}\right\}}{\text{Area exposed (square inches)} \times 10}$$

$$\left.\begin{array}{l}\text{ppm "Zonyl" RP solids}\\ \text{extracted at 10 ml.}\\ \text{per square inch}\end{array}\right) = \frac{\text{ppm F extracted at 10 ml. per square inch}}{0.534*}$$

*"Zonyl" RP solids contain 53.4% fluorine

The reporting of extraction of "Zonyl" RP solids adjusted to ppm in 10 milliters of solvent per square inch was the procedure used during consideration of Food Additive Petition No. 5B1747.

For the purpose of interpreting the data in Exhibits A and B, it is assumed that the maximum permissible extraction

of "Zonyl" RP solids is a concentration of 0.2 ppm. in 10 ml. per square inch for water and for heptane after correction by a factor of 5 for the latter solvent. This was the guideline used in establishing a regulation under the Food Additive Petition No. 5B1747.

A comparison of data obtained for Condition of Use D (hot filled below 150°F.) with Condition of Use E (room temperature filled and stored) showed that:

(1) Extractability by heptane was essentially the same for both conditions (D) and (E).

(2) Extractability by heptane under Condition D was essentially unchanged by a two fold extension of the extraction time.

(3) Extraction by water at Condition D was slightly greater for Condition D but at 0.13 ppm was well within the guideline.

(4) Extraction by water reached 0.2 ppm on doubling the time for Condition D.

All of the above conclusions apply to paperboard treated with 0.17 lbs. per 1,000 square feet of "Zonyl" RP solids.

A comparison of data obtained under Condition of Use C (hot filled above 150°F.) with Condition of Use E (room temperature filled and stored) showed that:

(1) Extractability by heptane was equivalent at a "Zonyl" RP solids content of 0.14 lbs. per 1,000 square feet for Condition C to 0.17 lbs. per 1,000 square feet for Condition E. The degree of extractability did not increase at the 0.14 lbs. per 1,000 square feet level on doubling the time of exposure for Condition C. An increase in solids content on the paperboard to 0.17 lbs. per 1,000 square feet led to a significant increase in the amount of "Zonyl" RP removed.

(2) Extractability by water under Condition C is less than under Conditions E or D. The exposure under Condition C is distinctly different in procedure since the cell is filled with boiling water and left to cool to 100°F. rather than holding for several hours at 150°F. or 24 hours at 120°F.

2. Abrasion Data

Data were not obtained since there is no need for treating paperboard used in packaging dry solids ~~con-~~ containing no free fat or oil.

3. End Test and Usage Specifications

It is requested that regulation 121.2526 be amended to delete the present listing of diethanolamine salts of mono and bis (1H, 1H, 2H, 2H perfluoroalkyl) phosphates, etc., and to substitute the following:

List of Substances

Diethanolamine salts of mono and bis (1H, 1H, 2H, 2H perfluoroalkyl) phosphates where the alkyl group is even numbered in the range C_8-C_{18} and the salts have a fluorine content of 52.4 to 54.4% as determined on a solids basis.

Limitations

For use only as an oil and water repellent at a level not to exceed 0.14 pound (0.075 pound of fluorine) per 1,000 square feet of treated paper or paperboard, without correction for any fluorine which might be present in the untreated paper or paperboard, when such paper or paperboard is used in contact with nonalcoholic foods under the conditions of use described in paragraph (C) of Section 121.2526, Table 2, Condition of Use (C), (D), (E), (F), and (G).

E. Methodology

The concentration of mixed perfluoroalkyl phosphates in the paperboard is determined by fluorine analysis. Combustion of the paperboard by the Wickbold Torch procedure (Orchem Method 9-8-1A) is followed by determination of the fluoride in the torch effluent by a spectrophotometric procedure (Orchem Method 6-11-34) or by the Fluoride Ion Activity Method (Orchem Method 2-10-6). Method 9-8-1A is an updated version with minor revisions of Method 9-8-1 used in Food Additive Petition No. 5B1747. Copies of Methods 9-8-1 and 6-11-34 were provided to the Food and Drug Administration by the letter of J. H. James to Willard G. Orr, dated February 16, 1967, and relating to Food Additive Petition No. 5B1747. Information and data for verification of the validity of these two methods was supplied to Food and Drug Administration by the letters of J. H. James to Willard G. Orr dated February 27, 1967 and March 23, 1967 and relating to Food Additive Petition No. 5B1747.

Copies are attached of the following methods:

Orchem Method No.	Title
9-8-1A	Microcombustion of Organic Materials - Wickbold Torch Method
6-11-34	Fluoride-Spectrophotometric Determination in Aqueous Solutions
2-10-6	Fluoride-Determination by Fluoride Ion Activity Electrode Method

In addition, copies are included of the following methods referred to in earlier sections:

Orchem Method No.	Title
2-10-10	Fluoride Determination by Standard Addition
2-74-1	Fluoride Determination by Thorium Nitrate Titration
90-9-4-1A	"Zepel" Polymers and Extender Polymers-Determination of Active Ingredient. (This is the identical procedure used to determine active ingredient in "Zonyl" RP).

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