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EUROPEAN PATENT APPLICATION

⑳ Application number: 83103896.7

⑤① Int. Cl.³: **C 07 C 69/76**
C 07 C 67/26, D 06 M 13/20

㉔ Date of filing: 16.04.83

③① Priority: 20.05.82 US 380188
30.08.82 US 412620

④③ Date of publication of application:
30.11.83 Bulletin 83/48

⑧④ Designated Contracting States:
DE FR GB IT

⑦① Applicant: **ALLIED CORPORATION**
Columbia Road and Park Avenue P.O. Box 2245R (Law
Dept.)
Morristown New Jersey 07960(US)

⑦② Inventor: **Oxenrider, Bryce Clifford**
41 Circle Road
Florham Park New Jersey 07932(US)

⑦④ Representative: **Baillie, Iain Cameron et al,**
c/o Langner Parry Isartorplatz 5
D-8000 München 2(DE)

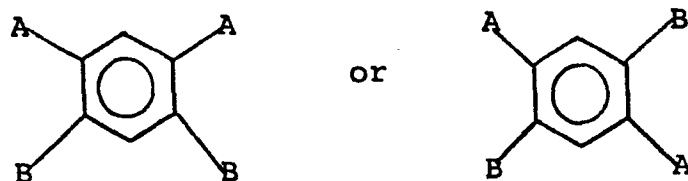
⑤④ Mixtures comprising fluorinated pyromellitate oligomers useful as surfactants and processes for the production and use thereof.

⑤⑦ A process is disclosed for producing organic oligomeric mixtures useful as fiber surface modifying agents. The process comprises reacting pyrometallitic dianhydride with fluorinated alcohols and oxirane compounds to produce organic mixtures containing more than one mole of groups derived from pyrometallic dianhydride per two moles of groups derived from fluorinated alcohol.

DESCRIPTIONMIXTURES COMPRISING FLUORINATED PYROMELLITATE
OLIGOMERS USEFUL AS SURFACTANTS AND PROCESSES
FOR THE PRODUCTION AND USE THEREOFBACKGROUND OF THE INVENTION

The present invention relates to a process for the production of highly effective surface treating agents. The surface treating agents produced in accordance with this invention comprise oligomeric mixtures containing pyromellitate nuclei. Many of the pyromellitate nuclei contain fluorinated ester moieties which impart water and oil repelling characteristic to various fibers.

U.S. Patent 4,209,610 (Mares et al., 1980) discloses fluorinated pyromellitates useful as surface modifiers for polyamides and polyesters. One preferred group of compounds in that patent are those of the formula:



wherein A is a fluorinated ester such as $\text{CF}_3(\text{CF}_2)_p\text{R}'\text{O}(\text{O})\text{C}-$ and wherein B is $\text{HOCH}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}(\text{O})\text{C}-$; wherein R' is ethylene and p is a mixture of integers such as 3, 5, 7, 9 and 11 for different chains. Such products are formed by the reaction of pyromellitic dianhydride with a fluorinated alcohol, and then the reaction of the product diacid/diester with epichlorohydrin. Specifically, the product is produced by reaction of two moles of fluorinated alcohol with each mole of

pyromellitic dianhydride to form the diacid/diester.

Each mole of the diacid/diester is then reacted with two moles of epichlorohydrin to produce the product.

Because the oxirane may react at the one or two carbon,
5 the product will normally contain minor amounts of material with B being $\text{HOCH}_2\text{CH}(\text{CH}_2\text{Cl})\text{O}(\text{O})\text{C}-$ (the product with a pendant primary alcohol) as well as major amounts of material with B being $\text{HOCH}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}(\text{O})\text{C}-$ (the product with a pendant secondary alcohol). Other patents relating
10 to the production of this product include U.S. Patent No. 4,252,982 (Oxenrider 1981) wherein an ester solvent is used and U.S. Patent 4,321,403 (Oxenrider et al., 1981) wherein N-methyl pyrrolidone is used as solvent. Methods for applying the compound in aqueous
15 emulsions to fibers are disclosed in U.S. Patent Nos. 4,192,754 (Marshall et al., 1980), 4,134,839 (Marshall, 1979), 4,190,545 (Marshall et al. 1980), 4,193,880 (1980), 4,283,292 (Marshall, 1981) and 4,317,736 (Marshall, 1982).

20 The pyromellitate oligomers of the present invention have extremely high resistance to soiling, and soil resistant properties imparted to fibers by the oligomers of this invention are retained by the fibers after numerous laundering cycles. Therefore, fibers treated
25 with the oligomers of the present invention will retain soil resistance properties for long periods of time in an environment where they are ultimately employed. Furthermore, as described in each of the above patents, an annealing step is employed after the application of the
30 compound to the fiber. It would be desirable to be able to lower the temperature of the annealing step, for energy savings, without impairing either the initial soil resistance or the retention of soil resistance after laundering. With some of the oligomeric product
35 mixtures of the present invention, the annealing step may be accomplished at temperatures as low as 50°C.

BRIEF DESCRIPTION OF THE INVENTION

The present invention relates to a process for the

production of an organic mixture useful as a fiber surface modifying agent by reaction of pyromellitic dianhydride, fluorinated alcohol and an oxirane compound selected from the group consisting of epichlorohydrin, epibromohydrin, and propylene oxide, characterized by the organic mixture containing more than one mole of groups derived from pyromellitic dianhydride per two moles of groups derived from fluorinated alcohol, and being either a first process of:

10 (a) reacting pyromellitic dianhydride with fluorinated alcohol at a mole ratio of two moles of fluorinated alcohol per mole pyromellitic dianhydride to produce a pyromellitate having two fluorinated ester moieties and two carboxylic acid moieties; and

15 (b) reacting said pyromellitate of step (a) with an excess of oxirane compound in the presence of additional pyromellitic dianhydride to produce said organic mixture comprising oligomeric compounds; wherein said oxirane compound reacts with said carboxylic acid moieties to produce an ester having a primary or secondary alcohol, and wherein said alcohol reacts with said additional pyromellitic dianhydride to produce ester-linking moieties and carboxylic acid moieties capable of reacting with said oxirane compound to produce additional esters having primary or secondary alcohols; or a second process of:

25 (a') reacting pyromellitic dianhydride with fluorinated alcohol at a mole ratio of fluorinated alcohol to pyromellitic dianhydride between 1:0.55 and 1:1.0 to form a partially esterified pyromellitate having fluorinated ester groups, free acid groups and anhydride groups; and

30 (b') reacting the partially esterified product with oxirane compound in an amount sufficient to cause essentially all of the free acid groups and anhydride groups to be esterified.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention utilized for

the production of oligomer-containing mixtures employs three) reactants. Pyromellitic dianhydride is one of the three reactants. Preferably, commercial grade pyromellitic dianhydride of greater than 98% purity should be employed for the practice of the present invention. Common impurities which can be tolerated in minor amounts include pyromellitic monoanhydride.

A second reactant is a fluorinated alcohol. While any alcohol having a relatively long chain of CF_2 groups with a terminal CF_3 group may be employed, the preferred fluorinated alcohols can be represented by the formula $\text{CF}_3(\text{CF}_2)_p\text{R}'\text{OH}$, wherein R' is alkylene of 2 to 6 carbons, and p is an integer between 3 and 15, preferably between 3 and 13. In that formula R' is preferably ethylene, 1,2-propylene or 1,4-butylene, and is most preferably ethylene. It is contemplated, and in fact preferred, to use a mixture of alcohols, particularly mixtures with the same R' group such as ethylene, but with varying values for p . A representative commercial mixture of fluorinated alkyl ethanols has the formula $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ wherein n is, predominantly, 2, 3 and 4, with lesser amounts of n being 1 and 5, and traces only of n being 6 or 7.

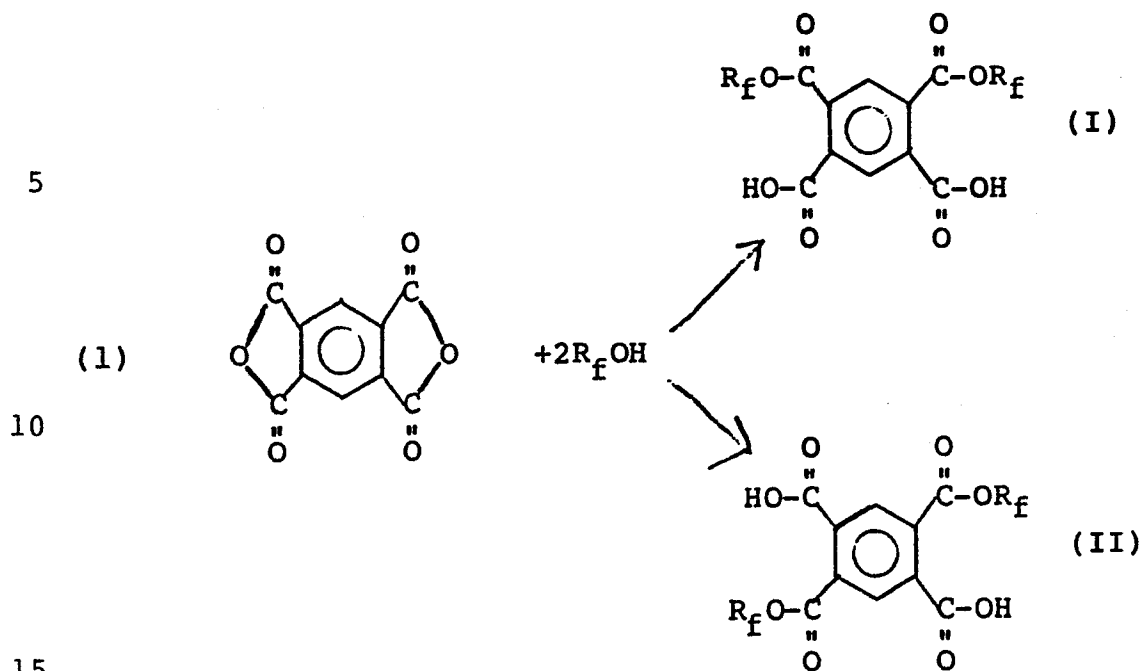
A third reactant used in the present process is preferably epichlorohydrin. It may also be the corresponding bromo compound, known as epibromohydrin or propylene oxide. It will be appreciated that all three of these compounds are three carbon oxiranes with the third carbon being of the formula CH_2X wherein X is Cl , Br or H .

The process of this invention may be conducted in any of the organic solvents utilized in forming the compounds of Mares et al., Oxenrider et al., or Oxenrider. Illustrative examples of useful solvents include dimethylformamide, N-methylpyrrolidone and aliphatic esters having a boiling point below about 150°C , such as methyl acetate, ethyl acetate, propyl acetate, etc. Other suitable solvents include aliphatic ketones

such as methyl isobutyl ketone. The preferred solvent for the practice of this invention is N-methylpyrrolidone.

The process of this invention produces organic oligomeric mixtures useful as fibers surface modifying agents. The process comprises reacting pyromellitic dianhydride with the above-described fluorinated alcohols and oxirane compounds to produce organic mixtures containing more than one mole of groups derived from pyromellitic dianhydride per two moles of groups derived from fluorinated alcohol. The process of the invention may be conducted via two modes as described hereinbelow, with the first mode being the preferred method of practicing the invention.

The order of reaction for the first mode of this invention is to initially react the fluorinated alcohol with pyromellitic dianhydride to produce a pyromellitate intermediate having two fluorinated ester moieties and two free acid moieties. The ratio of the reactants employed in the production of the diester/diacid intermediate should be two moles of fluorinated alcohol per mole of pyromellitic dianhydride. This initial reaction may be conducted at temperatures between 20°C and 80°C with 45°C being the preferred temperature for this step of the process. The length of this initial reaction will range from 2 hours to 40 hours depending upon the reaction temperature and whether a catalyst such as triethylamine is employed. Higher reaction temperatures and catalysts will enhance the rate of the reaction and consequently, reduce the time required for the reaction to occur. The diester/diacid intermediate produced via the reaction of a mole ratio of fluorinated alcohol to pyromellitic dianhydride of 2:1 is the same intermediate produced in the above Mares et al., Oxenrider et al., and Oxenrider patents. The described first step of the first mode of this invention may be illustrated by reaction (1) as follows:

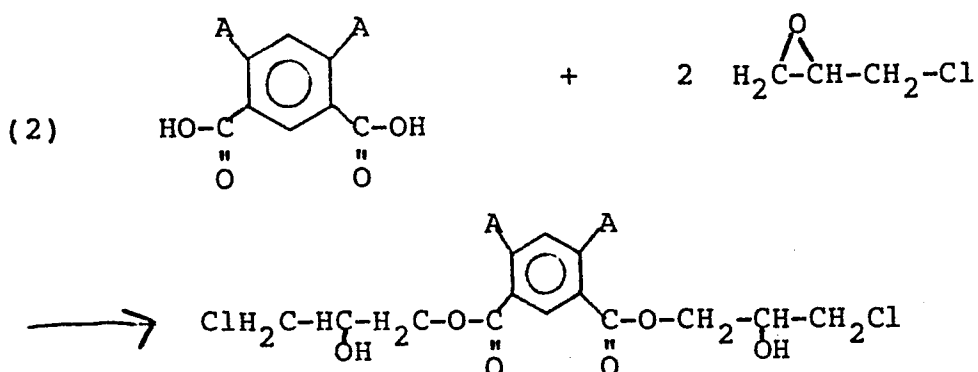


wherein R_fOH is a fluorinated alcohol as described hereinbefore.

The diester/diacids represented by structures (I) and (II) above depict the meta and para isomers. It should be appreciated that the diester/diacid intermediate will actually constitute a mixture of the meta and para isomers. It is not necessary to isolate the diester/diacid before proceeding to the next step or steps of the first method of practicing this invention. However, the diester/diacid could be isolated if it was desired to do so.

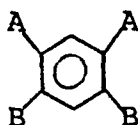
Following production of the diester/diacid pyromellitate intermediate, an excess of the third reactant, an oxirane compound as described above, is added to the reaction medium. The excess of oxirane employed will be more than two moles of oxirane compound per mole of pyromellitic dianhydride utilized in the first step of the process. As will become apparent, the amount of excess of oxirane compound employed will depend somewhat upon the amount of pyromellitic dianhydride added to the reaction medium in a later step. The oxirane compound will react with the free acid moieties of the diester/diacid intermediate to produce a pyromellitate tetra-

ester having two fluorinated ester moieties and two ester moieties having a primary or secondary alcohol. Production of the ester moiety having a primary or secondary alcohol results from the reaction of the oxirane compound at the 1 or 2 carbon with a free acid group. For example, reaction (2) below illustrates the reaction between epichlorohydrin and the diester/diacid intermediate.



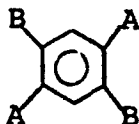
(III)

In reaction (2), A is a fluorinated ester moiety as previously described. In structure (III), the ester group containing the alcohol will now be referred to as B. Therefore, structure (III) may be illustrated as follows:



(IV)

As previously stated, the para isomer of the diester/diacid intermediate is also formed. Therefore, structure (III) may also take the following form:



5

(V)

It should also be appreciated that if the oxirane compound reacts at the number 2 carbon, the B group will take the form of $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-CH-CH}_2\text{OH}$. However, B groups

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having a primary alcohol are believed to represent only 10% of the total number of B groups which are formed.

The reaction between the diester/diacid intermediate and the oxirane compound, reaction (2), should be conducted at a temperature between 20°C and 90°C with 55°C being the preferred temperature for this step of the first mode of this invention.

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The temperature for the second step will be that necessary to achieve the desired level of conversion (as measured by the disappearance of free carboxyl groups), such desired level being discussed below. Representative times for the second step are 4 to 20 hours, which may overlap with the third step as discussed below.

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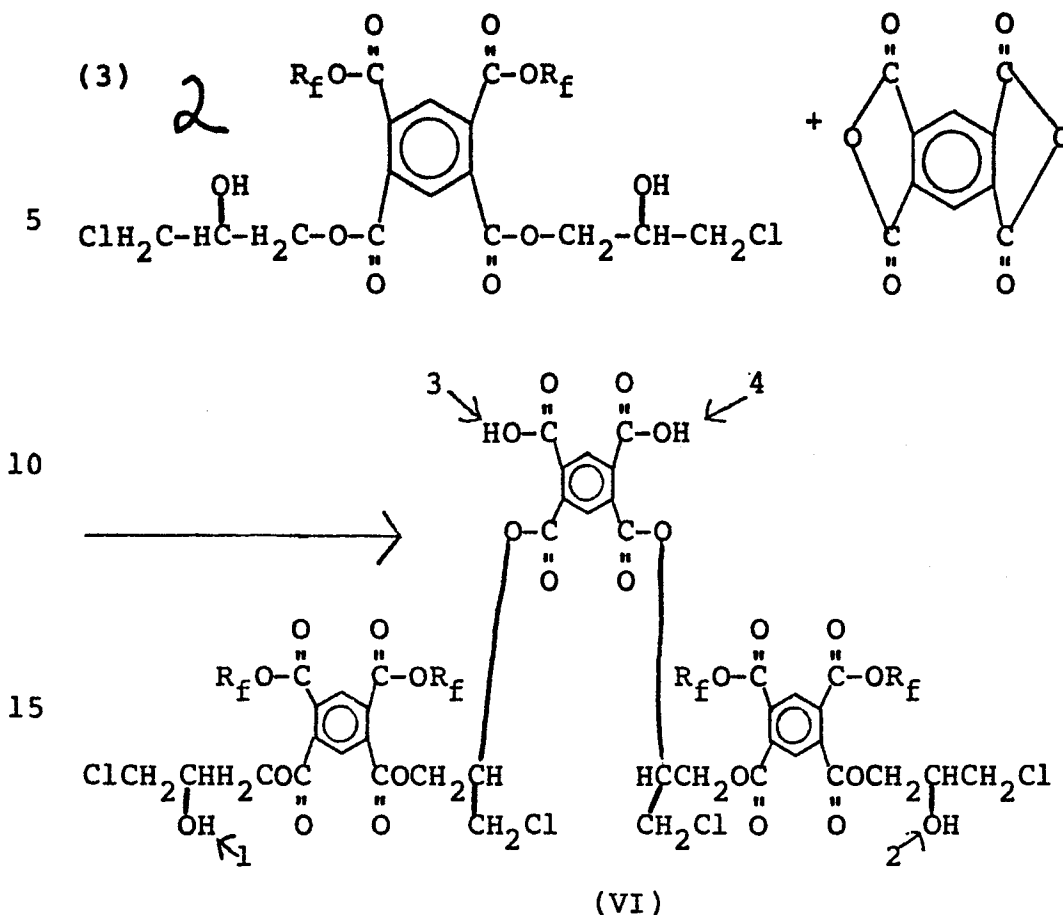
Reaction (2), the second step of the process, should preferably be conducted in the presence of a catalyst. Suitable catalysts include triethylamine, tributylamine, lutidine, pyridine and the like with triethylamine being the preferred catalyst.

25

The next reaction necessary for the practice of the process involves the reaction of a B group primary or secondary alcohol of structure IV or V with an anhydride moiety of pyromellitic dianhydride. Reaction between said alcohol moieties and said anhydride moieties produces an ester linking group and a free acid group. This reaction may be illustrated as follows by the reaction of two pyromellitate tetraesters produced in accordance with this invention with a molecule of pyromellitic dianhydride:

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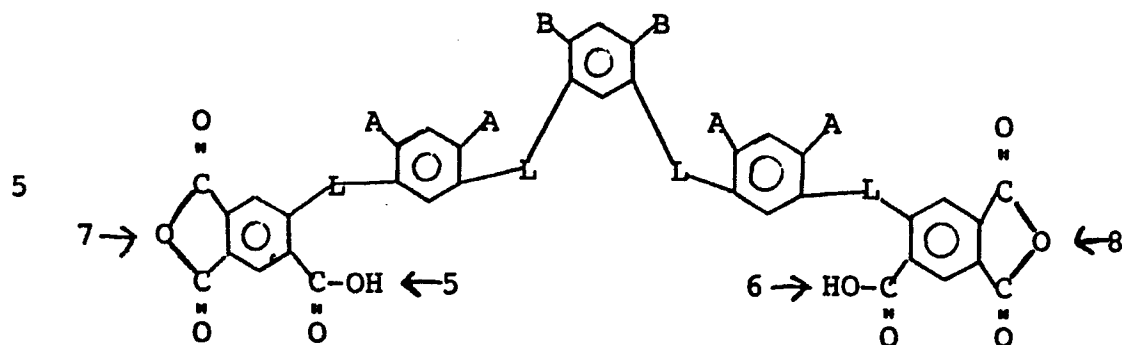
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In order for reaction (3) to occur, additional pyromellitic dianhydride must be added to the reaction medium after the formation of the diester/diacid in reaction (1). The pyromellitic dianhydride may be added to the reaction medium simultaneously with the addition of the oxirane compound. When this procedure is followed, as soon as free acid groups are esterified by the oxirane compound thereby forming B groups containing a primary or secondary alcohol, the alcohol may react with an anhydride moiety in accordance with reaction (3) as described. It is especially preferred, however, to monitor reaction (2) by the disappearance of carboxyl groups via standard titration techniques and to add additional pyromellitic dianhydride to the reaction medium when 50% to 100% of the free acids have been esterified. It is especially preferred to add additional pyromellitic dianhydride to the reaction mixture when 85% to 95% of the carboxyl groups have been esterified as determined by titration procedures.

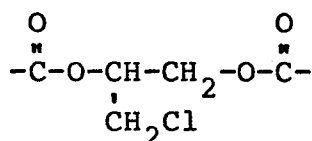
As described, once excess pyromellitic dianhydride is added to the reaction medium, reaction (3) of the process of this invention will occur if ester groups having a primary or secondary alcohol (B groups) are present. Reaction (3) will occur at temperatures between 20°C and 90°C with 55°C being the preferred temperature for reaction (3). Completion of reaction (3) will be evidenced by the disappearance of essentially all unreacted carboxyl groups. The determination that essentially no unreacted carboxyl groups remain may be accomplished by standard titration procedures. The time required to complete reaction (3) will range from 1 hour to 40 hours, depending upon the reaction temperature, amount of additional pyromellitic dianhydride employed, etc. It is believed that higher temperatures for reaction (3) will drive the process to form higher oligomers than would be produced by lower reaction temperatures.

Examination of structure VI reveals that structure VI has four hydroxyl groups (1, 2, 3, and 4 as labeled) which are capable of undergoing a further reaction. Hydroxyls 1 and 2 are capable of reacting with an anhydride moiety of an unreacted pyromellitic dianhydride molecule to form additional ester linking groups and free acid groups. Hydroxyls 3 and 4 are capable of reacting with unreacted oxirane compound to form additional B groups having the B group structure previously described (i.e., ester groups having a primary or secondary alcohol). The organic structure formed by the reaction of the four hydroxyls of structure VI is a pentamer represented by structure VII as follows:



(VII)

10 wherein A and B are as previously described and L is an ester linking group having the following structure:



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It should be appreciated that chlorine in the above structure could alternately be bromine or hydrogen if epibromohydrin or propylene oxide were to be employed in place of epichlorohydrin.

20

Structure VII contains two hydroxyls (5 and 6 as labeled) and two anhydride groups (7 and 8 as labeled). Hydroxyls 5 and 6 will react with the oxirane compound to produce additional B groups capable of reacting with another anhydride, and anhydrides 7 and 8 of structure VII will react with an alcohol from an 8 group of a fluorinated pyromellitate or a 2 group from another anhydride to form additional ester linking groups (L groups as described for structure VII).

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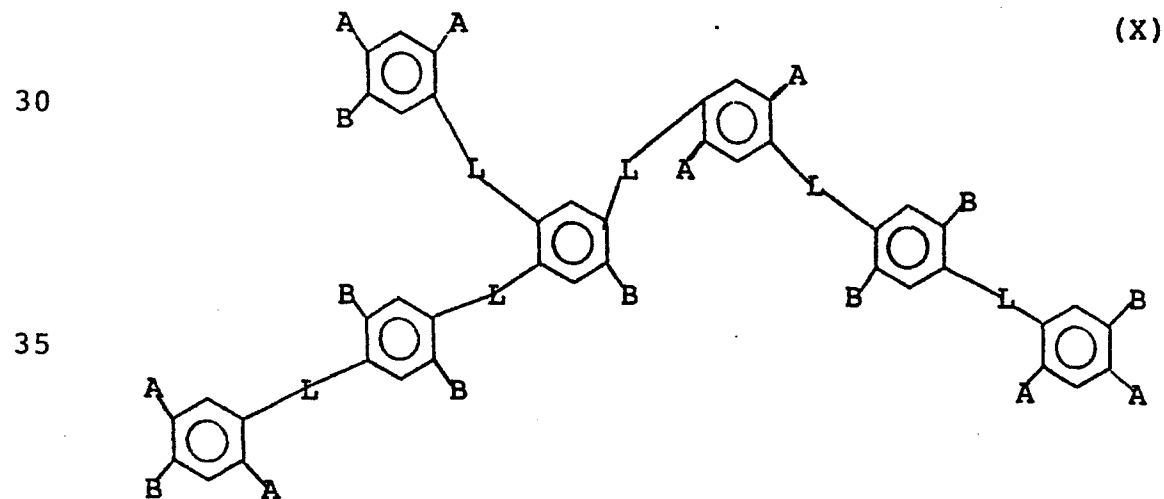
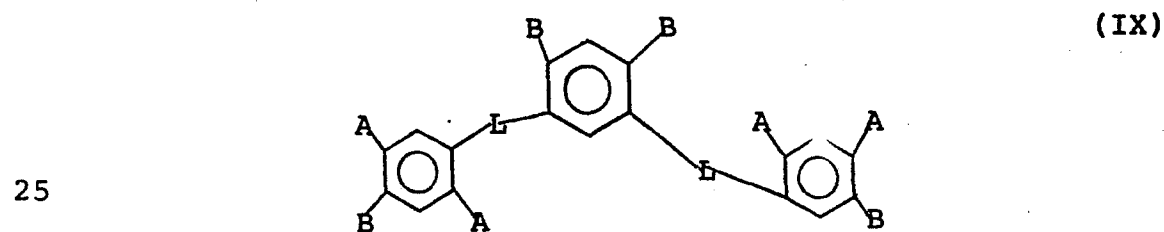
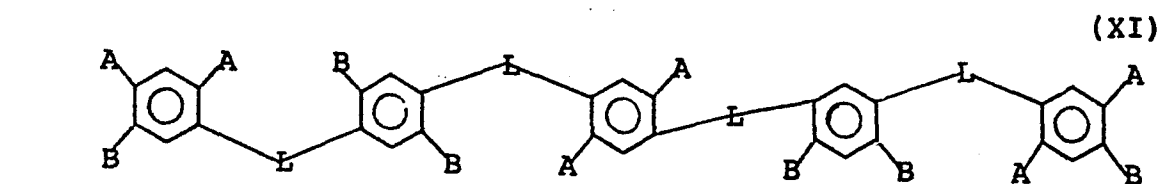
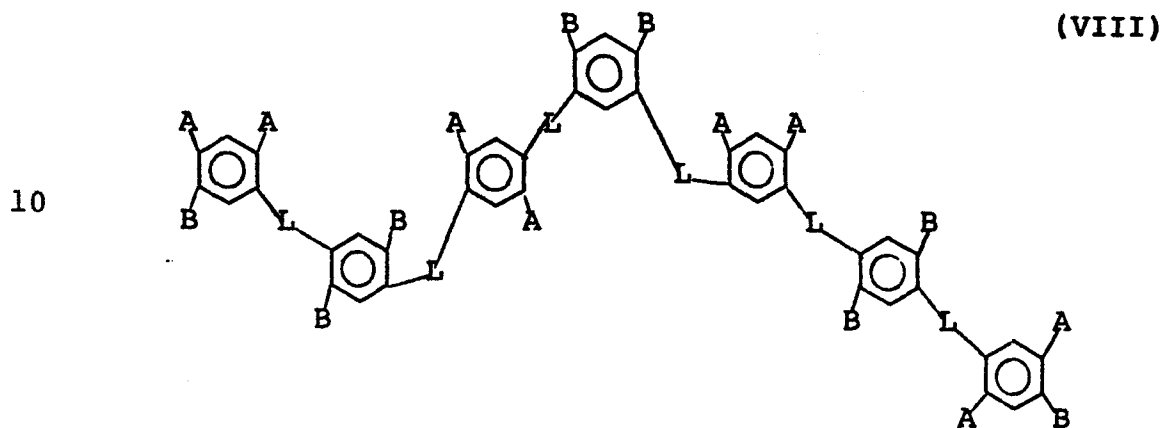
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It should be appreciated that structures VI and VII are intermediates in the oligomerization process because the oligomeric product mixture will contain essentially no unreacted acid or anhydride groups. The exact path the oligomerization process will travel is uncertain, and an undeterminable number of oligomeric species in an undeterminable ratio will inherently result in the oligomeric product mixture.

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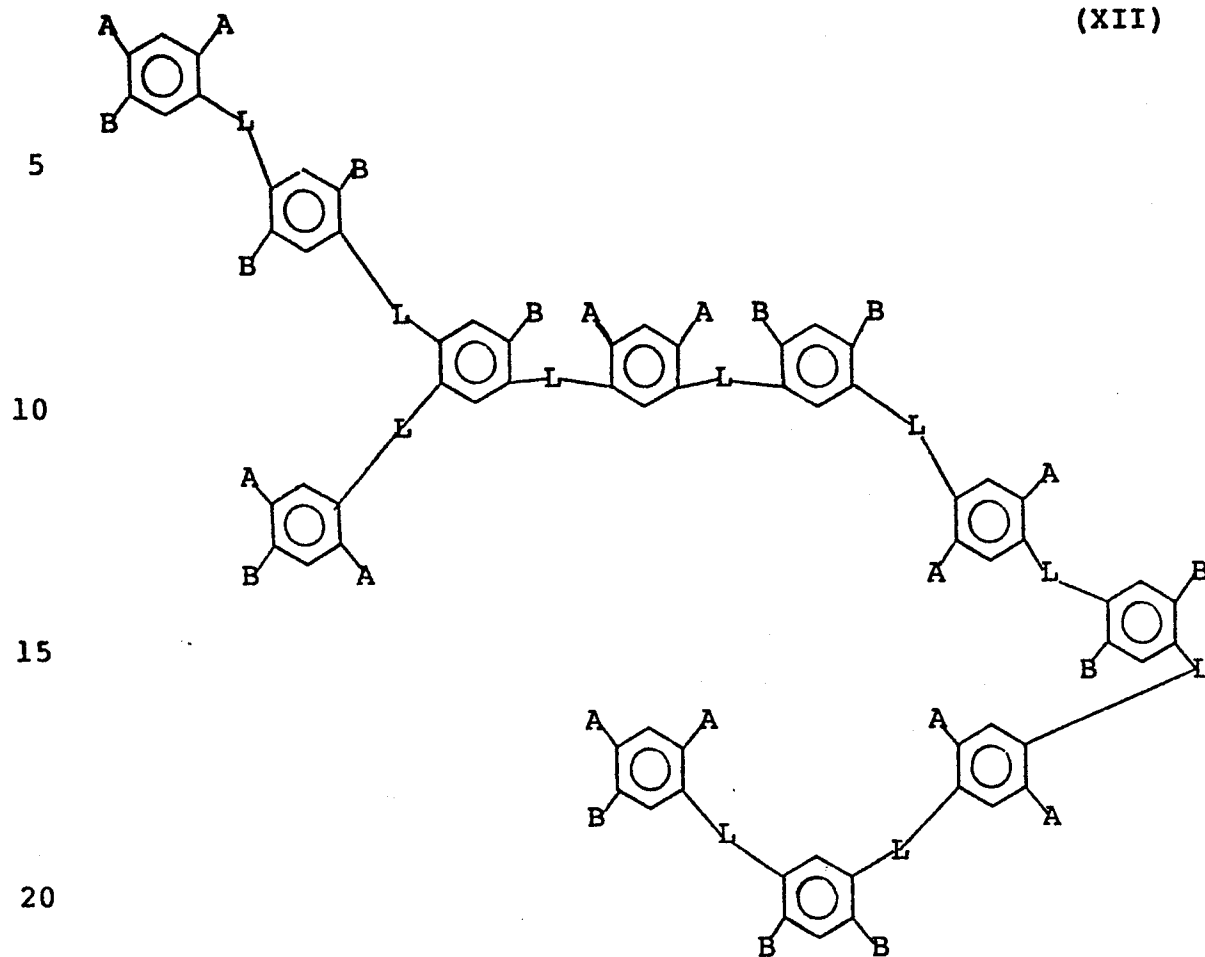
For illustrative purposes, structures VIII through XIII below represent oligomers which may be present in

the oligomeric product mixture produced by the first mode of this invention. Structures VIII through XIII are intended to illustrate, but not to exhaust, the oligomeric components of the novel mixture produced by the first mode of practicing the present invention.

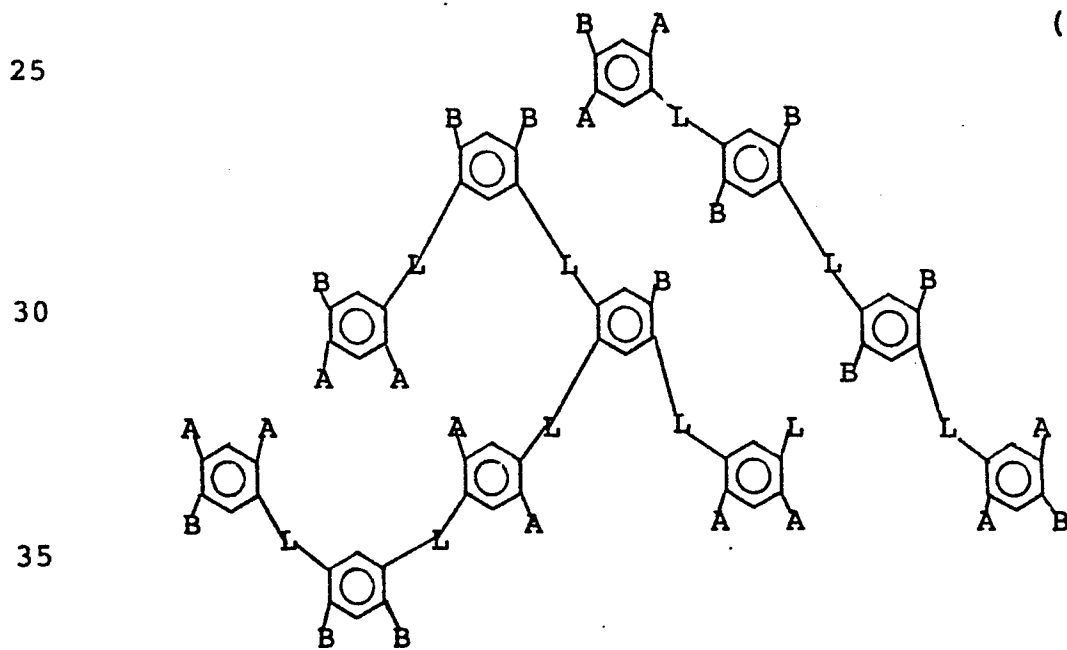


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(XII)



(XIII)



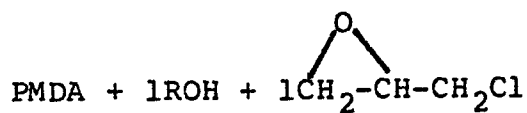
In structures VIII through XIII, A represents a fluorinated ester group as previously described; B represents an ester group having a primary or secondary alcohol as previously described; and L represents an ester linking group as previously described.

The second mode of practicing the present invention involves reacting pyromellitic dianhydride with fluorinated alcohol at a mole ratio of fluorinated alcohol to pyromellitic dianhydride between 1:0.55 and 1:1.0 to produce a partially esterified pyromellitate having fluorinated ester groups, free acid groups and anhydride groups. The pyromellitate is then reacted with an oxirane compound in an amount sufficient to cause essentially all of the free groups to be esterified.

The order of reaction for the second mode of the present process is to first react the fluorinated alcohol with pyromellitic dianhydride and then react the oxirane compound with the intermediate. Taking the simplest case of one mole of fluorinated alcohol for each mole of pyromellitic dianhydride, the product will, on average, have only one fluorinated ester group on a pyromellitate, the adjacent position on the pyromellitate being free acid and the two other positions (the 4-carbon and the 5-carbon of the ring) still linked by anhydride. It will be appreciated, however, that this product represents only an average, with the actual reaction mixture containing some unreacted pyromellitic dianhydride some of this acid/ester/anhydride and some diester/diacid. In the absence of steric factors or other considerations affecting reaction rate, one would expect a distribution of these three products of 1:2:1 when one mole of fluorinated alcohol is used for each mole of pyromellitic dianhydride. The use of more than one mole of fluorinated alcohol per mole of pyromellitic dianhydride would be expected to increase the amount of diacid/diester in the product, while the use of less

than one mole of fluorinated alcohol per mole of pyromellitic dianhydride would be expected to decrease the amount of diester/diacid in the product with a resultant increase of unreacted pyromellitic dianhydride.

5 The second step of the second mode of practicing the present invention for producing fiber surface treating agent involves reaction of the above intermediate with the oxirane compound, e.g. epichlorohydrin. It will be appreciated that the oxirane group of epichlorohydrin is capable of esterifying free acids, but cannot esterify anhydrides. Accordingly, the initial reaction in the second step will be between the oxirane group and those free carboxylic acids present in the intermediate, liberated as a result of the first step. This reaction product is illustrated by formula XIV that follows, with the ester/acid of the pyromellitate on the right converted to a product (at least as to these two ring sites) identical to the product of the Mares et al. patent. The anhydride of the pyromellitate on the left, however, cannot react directly with epichlorohydrin or any of the other oxirane compounds (epibromohydrin and propylene oxide). Accordingly, it reacts with the free secondary (or sometimes primary) alcohol formed on the pyromellitate on the right. This reaction is illustrated by the transition from formula XIV to formula XV wherein the epichlorohydrin esterfied group forms a linking group between the two rings by proton transfer to the linking oxygen of the anhydride group. Since this new intermediate XV has a free carboxylic acid group, it may now react with epichlorohydrin so as to produce the final product XVI.



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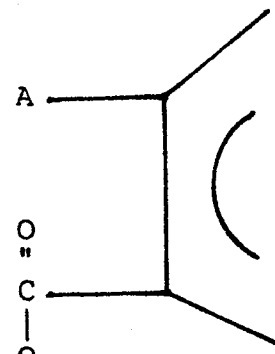
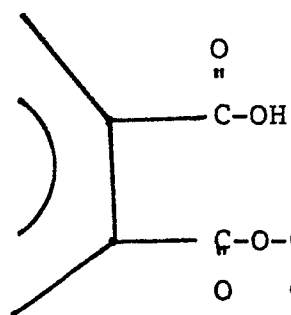
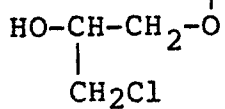
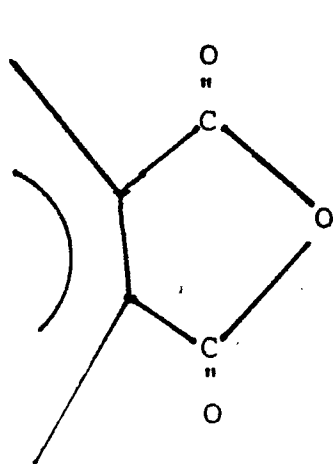
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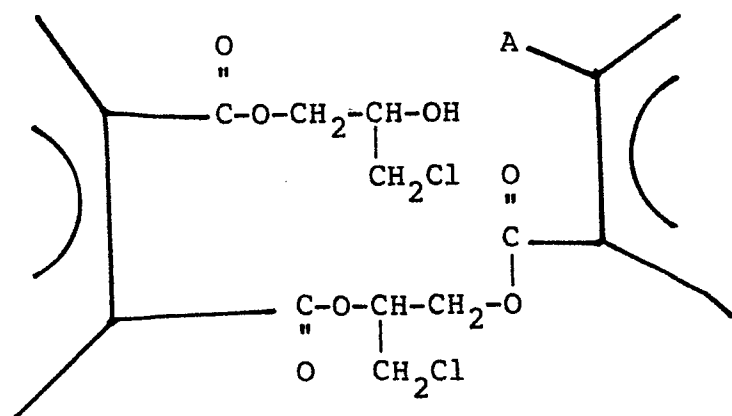
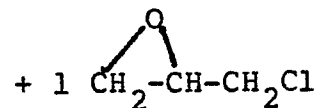
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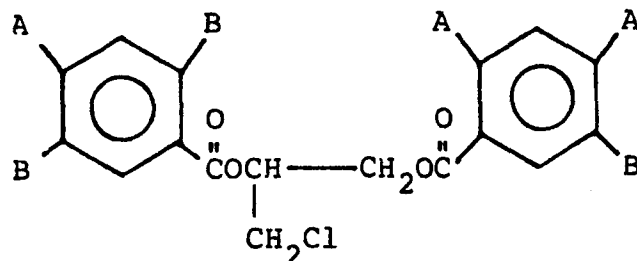
(XIV)

(XV)



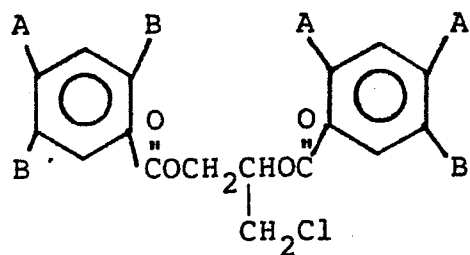
(XVI)

It should be appreciated that the reaction illustrated by formulae XIV, XV and XVI is only representative of the kinds of reactions that can occur in the second mode of the present process when the oxirane compound is added to an intermediate formed by reaction of pyromellitic dianhydride with less than two moles of fluorinated alcohol. Since the intermediate reaction product will contain a mixture, even with this single type of linking reaction, a mixture of products will result having a variety of structures. Thus, for example, if a mole of unreacted pyromellitic dianhydride is subjected to that reaction, it will be linked to at least two other pyromellitate rings in the manner shown in formula XVI. This alone will cause a plurality of dimers, trimers, tetramers, etc. to be formed, with predominant species being dimer and trimer so long as the proportion of unreacted pyromellitic dianhydride in the first reaction product is relatively small. Furthermore, since a small proportion of the oxirane compound normally reacts to produce free primary alcohol (with the carboxyl of the ring linked to the 2-carbon rather than to the 1-carbon), more than one linking structure between rings will be formed on the reaction with unreacted anhydride groups. It is believed that the linking structures will be $-C(O)OCH(CH_2Cl)CH_2OC(O)-$ in both instances, but that the structure will be reversed in direction when the pendant alcohol is primary. Some of the more common dimers and trimers are illustrated as formulae XVII through XXVI:



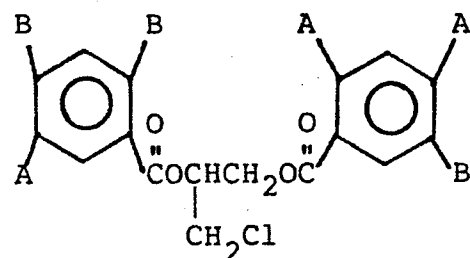
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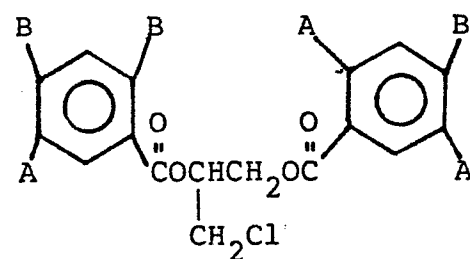
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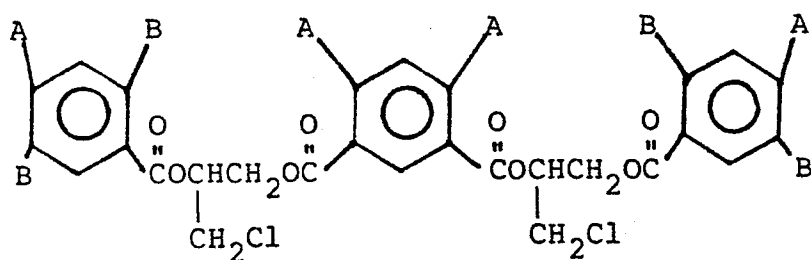
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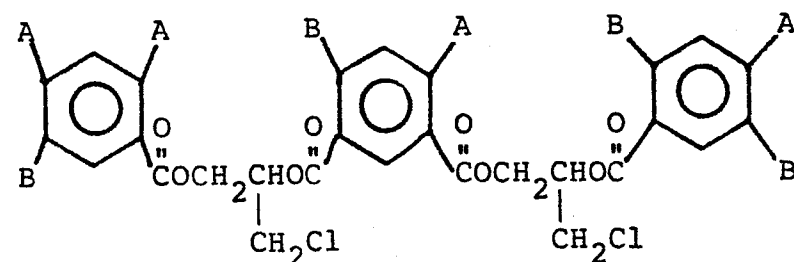
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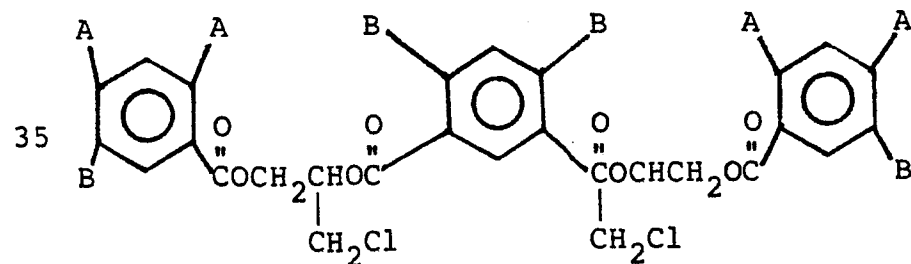
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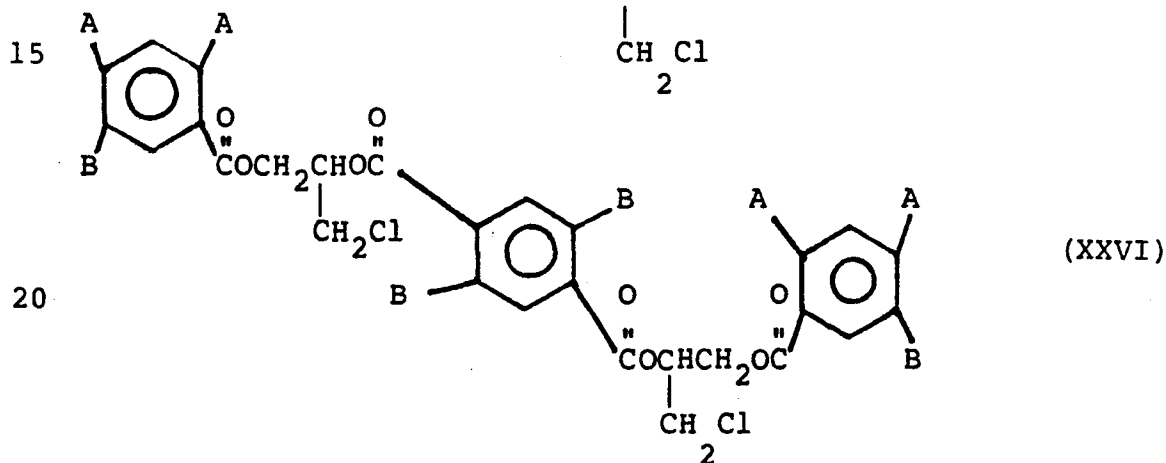
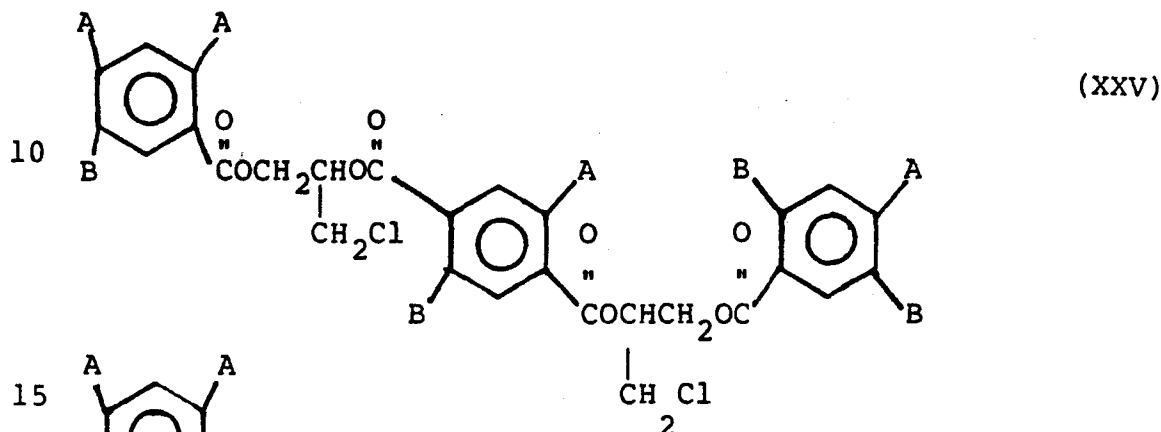
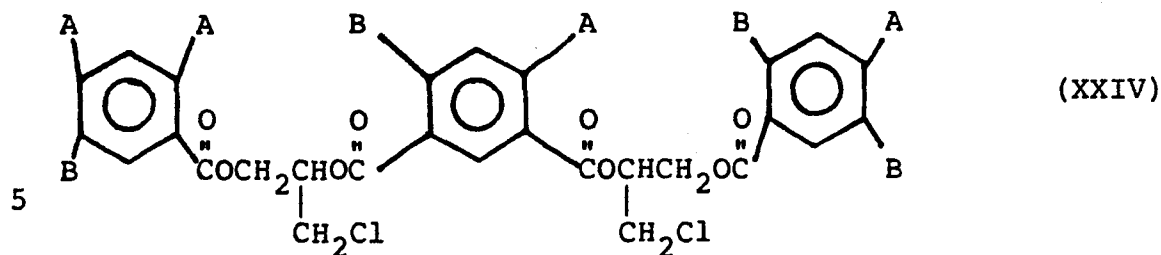
(XXII)

30



(XXIII)

35



25 In all of these formulae, A represents $-C(O)OCH_2CH_2(CF_2CF_2)_mCF_2CF_3$ and B represents a major proportion of $-C(O)OCH_2CH(CH_2Cl)OH$ and a minor proportion (10%) of $-C(O)OCH(CH_2Cl)CH_2OH$.

30 Formulae XVII-XXVI are intended to illustrate, but not by any means exhaust, the oligomeric components of the novel mixture produced by the second mode of the present process. It is further contemplated that the same or similar oligomers to those listed may have been present, intentionally or inadvertently, in commercially prepared mixtures within the scopes of the Mares et al. patent, but not in the same combinations and/or proportions as are produced by the present process. Furthermore, the desirability of at least some of these compon-

35

ents has been appreciated in a commonly assigned,
copending application of Thomas et al., Serial No.
350,544, filed February 19, 1982.

In the four dimers shown in formulae XVII-XX, the
5 linking groups originated from anhydrides on the left
ring and acid/ester on the right ring. In formulae
XVII, XIX and XX the epichlorohydrin reacted with the
free acid in the right ring to product pendant secondary
alcohol, which then reacted with anhydride on the left
10 ring. In formula XVIII epichlorohydrin reacted with the
free acid on the right ring to produce pendant primary
alcohol, which then reacted with anhydride on the left
ring.

In the six trimers shown in formulae XXI-XXVI, the
15 initial acid/ester groups were on the left side of the
left ring; the right side of the right ring and the two
interior positions where the A's are present in each
formula. The reaction involves two monoanhydrides in
XXI, XXII, XXIV, and XXV and involves one dianhydride in
20 XXIII and XXVI.

In all cases the free acids reacted with epichloro-
hydrin to produce pendant primary or secondary alco-
hols. The pendant alcohols then reacted with anhydrides
on adjacent rings to produce the linkages shown and free
25 carboxyls, which then reacted with epichlorohydrins to
produce "B" groups.

As indicated above, any of the preferred solvents
useful in forming the compounds of Mares et al.,
Oxenrider et al. and Oxenrider may be used in the pre-
30 sent invention, such as dimethylformamide, N-methyl-
pyrrolidone and aliphatic esters boiling below 150°C
(such as ethyl acetate and butyl acetate). Other suit-
able solvents include aliphatic ketones such as methyl
isobutyl ketone.

35 Catalysts and particularly acid acceptors such as
triethylamine, may be employed in the second mode of the
present process, particularly in the second step.

The temperatures for the two steps of the reaction

are not critical. It is preferred that the temperature during the first step be between 15°C and 80°C (more preferably 40°C to 50°C). It is preferred that the temperature during the second step be between 45°C and 100°C (more preferably 50°C to 75°C). The reaction times are not critical, but it is preferred that the first step be run long enough to react essentially all (e.g. 90% or greater) of the fluorinated alcohol introduced and that the second step be long enough to react essentially all free carboxyls (e.g. until at least 90%, or more, preferably at least 95%, of the free carboxyls titratable by alcoholic KOH are consumed).

As indicated above, the mole ratio of fluorinated alcohol to pyromellitic dianhydride in the first step of the second mode of the present invention is between 1:0.55 and 1:1.0. Preferably this ratio is between 1:0.6 and 1:0.85, and more preferably it is between 1:0.65 and 1:0.75. As illustrated by the examples below, maximum retention of oil repellency, especially at annealing conditions between 100°C and 130°C, are achieved with the preferred and more preferred mole ratios of fluorinated alcohol to pyromellitic dianhydride.

For both modes of practicing the invention, it is desirable to conduct the process in a dry atmosphere, as for example, in the presence of dry nitrogen. Pressure is not critical, with atmospheric pressure being suitable. Solvent amounts are not critical, with sufficient solvent being enough to keep at least half of the pyromellitates and fluoroalcohols in solution (since precipitates can redissolve into solution as it reacts), and preferably all of the reactants, intermediates, and products in solution.

Once formed, the oligomer-containing mixtures of the present invention are normally recovered from the solvent in a manner analogous to that employed in the above Mares et al., Oxenrider et al. and Oxenrider patents. Thus, for example, the entire reaction mixture

may be added to a non-solvent such as water when N-methylpyrrolidone is used as solvent, or a volatile ester or ketone solvent may be distilled from the reaction mixture. In either case, it is preferred to wash
5 the initial product at least once with water in order to remove any remaining solvent and/or catalyst and/or unreacted reactants, and especially unreacted oxirane compounds.

The product may then be applied to the polyamide or
10 polyester fiber from an organic solvent such as acetone, methanol or dioxane. It is believed that the oligomeric product mixtures can be applied to fibers in an emulsion similar to the emulsion described in U.S. Patent No. 4,192,754 Marshall et al., or in other emulsion systems
15 such as those described in the other Marshall and Marshall et al. patents listed above. It is also believed that the compound may further be applied to the fiber along with other fiber treating agents, and especially spin finishes used to reduce friction of the
20 fiber during processing.

Suitable fibers include poly(caproamide) (nylon 6), poly(hexamethylene diamine adipate) (nylon 66) and other polyamides of both the poly(amino acid) type and poly-(diamine dicarboxylate) types such as poly(hexamethylene
25 diamine sebacate) known as nylon 6,12. Also suitable are polyesters such as poly(ethylene terephthalate) (PET). Levels of application are not critical, with levels on a fluoride/fiber basis similar to the above patents being suitable (e.g. 0.075-0.25% fluoride).

30 Subsequent to fiber application, it is preferred that the treated fiber be annealed to improve the adherence of the treating agent to the fiber. Annealing conditions are generally between 80°C and 160°C; but with the present products, the annealing temperature range is
35 from 40°C to 160°C. The oligomeric mixtures produced by the first mode of the present invention are especially unusual in that fibers treated with the mixtures exhibit excellent soil resistance properties and retention of

the properties, even though annealing temperatures as low as 40°C to 50°C are employed. However, in many preferred embodiments of this invention, the annealing step is conducted at temperatures between 100°C and 140°C.

5

EXAMPLES

Examples 1-13 more particularly illustrate the first mode of practicing the present invention. This mode is described on pages 5-14 of this application.

10 Examples 16-30 more particularly illustrate the second mode of practicing the present invention. The second mode is described on pages 14-21 of this application.

EXAMPLES 1-13

In performing the reactions described by Examples
15 1-13, a 500 mL or 250 mL 3-necked round bottom flask was fitted with a stirring bar, thermometer, water condenser, nitrogen inlet and vent. In each example, perfluoroalkylethanol refers to a mixture of fluorinated alcohols of the formula $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with $n =$
20 2, 3, 4 and 5. The fluorinated alcohols contained 2.1 meq OH/g.

EXAMPLE 1

Di-(perfluoroalkylethanol)-bis-(3-chloro-2-hydroxypropyl) tetraester of pyromellitic acid (40 g, 30.08
25 meq) was dissolved at 45°C in dry N-methylpyrrolidone (35 mL). Pyromellitic dianhydride (3.28 g, 30.11 meq) was added and the reaction mixture was allowed to react for 15 hours at 45°C. The temperature of the reaction mixture was raised to 55°C. Epichlorohydrin (7.05 mL,
30 90.24 meq) and triethylamine (0.13 mL) were added. The reaction mixture was then allowed to react for 13 additional hours. Upon cooling to room temperature, the reaction mixture was then poured into two liters of well-stirred ice water (5°C) to precipitate the product
35 and stirred for 0.5 hours. The precipitate was washed three more times in a similar manner. The product was recovered by filtration and dried overnight at room temperature under vacuum. An off-white solid product

weighing 34.7 g was recovered. The product had a surface energy of 10 dynes/cm as determined by the Zisman technique. Proton NMR confirmed the structural characteristics of the oligomeric product mixture.

5

EXAMPLE 2

Perfluoroalkylethanol (165.4 g, 347.34 meq), pyromellitic dianhydride (37.9 g, 347.92 meq) and N-methylpyrrolidone (160 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was
10 heated to 45°C and stirred for 18 hours in order to complete the initial reaction. The temperature of the reaction mixture was raised to 55°C and epichlorohydrin (81.5 mL, 1043.2 meq) and triethylamine (1.45 mL) were added to the reaction mixture. The reaction was con-
15 tinued for 5 additional hours. Pyromellitic dianhydride (19 g, 174.42 meq) was then added to the reaction mixture and the reaction was allowed to continue for 16 hours. The reaction mixture containing the product was allowed to cool to room temperature and was poured into
20 three liters of ice water (5°C). The product was washed and recovered as in Example 1. The product (240.9 g) was a tan, tacky solid and had a surface energy of 12 dynes/cm as determined by the Zisman technique. The structural characteristics of the product were confirmed
25 by proton NMR.

EXAMPLE 3

Perfluoroalkylethanol (159 g, 333.9 meq) pyromellitic dianhydride (36.4 g, 334.2 meq) and N-methylpyrrolidone (168 mL) were added to a reaction flask and reacted
30 as in Example 2. Epichlorohydrin (78.3 mL, 1002.24 meq) and triethylamine (1.5 mL) were added to the reaction mixture and the reaction was allowed to continue for 5 additional hours. Pyromellitic dianhydride (21.8 g, 200.12 meq) was added to the reaction mixture and the
35 reaction was completed as in Example 2. A tan solid product weighing 246.9 g was recovered via the procedure described in Example 1. The product had a surface tension of 12 dynes/cm as determined by the Zisman tech-

nique.

EXAMPLE 4

Using the procedures of Example 2, the following amount of reactants, catalyst and solvent were employed in order to produce an oligomeric mixture:

	Perfluoroalkylethanol	171.9 g	360.99
	Pyromellitic dianhydride	39.3 g	360.774
	(initial reaction)		
10	N-methylpyrrolidone	184.0 mL	
	Triethylamine	1.5 mL	
	Epichlorohydrin	84.7 mL	1084.16
	Pyromellitic dianhydride	35.5 g	234.09
15	A tan solid product (277.6 g) having a surface energy of 12 dynes/cm was recovered. Structural characteristics were confirmed by proton NMR.		

EXAMPLE 5

Perfluoroalkylethanol (160.3 g, 336.63 meq), pyromellitic dianhydride (36.7 g, 336.91 meq), and N-methylpyrrolidone (160 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was reacted at a temperature of 45°C for 23 hours. Epichlorohydrin (79 mL, 1011.2 meq) and triethylamine (1.4 mL) were added to the reaction mixture and the reaction was allowed to continue at 55°C for a period of 9.5 hours. By titration with alcoholic potassium hydroxide, it was determined that 91.5% of the carboxyl groups had reacted. Pyromellitic dianhydride (18.4 g, 168.91 meq), epichlorohydrin (39.5 mL, 505.6 meq) and triethylamine (0.7 mL) were then added to the reaction mixture. The reaction was continued for an additional 9.5 hours. Titration indicated that essentially all of the carboxyls had reacted at this point. A product weighing 235.4 g was recovered as in Example 1. Proton NMR confirmed the desired structural characteristics.

EXAMPLE 6

0095036

Perfluoroalkylethanol (164.5 g, 345.45 meq), pyromellitic dianhydride (37.7 g, 346.09 meq) and N-methylpyrrolidone (166 mL) were added to a reaction flask to
5 form a reaction mixture. The reaction mixture was allowed to react for 22 hours at 45°C. Epichlorohydrin (81 mL, 1036.8 meq) and triethylamine (1.44 mL) were added to the reaction mixture, and the reaction was continued at 60°C for 7.5 hours. Utilizing the titration
10 procedure described in Example 5, it was determined that 95% of the carboxyl groups had reacted. Pyromellitic dianhydride (18.8 g, 172.58 meq), epichlorohydrin (41.6 mL, 172.5 meq), and triethylamine (0.72 mL) were then added to the reaction mixture, and the reaction was con-
15 tinued for an additional 6 hours. Titration indicated that essentially all of the carboxyl groups had reacted. A product weighing 226.1 g was recovered as above. The product had a surface energy of 12 dynes/cm.

EXAMPLE 7

Perfluoroalkylethanol (162.7 g, 341.67 meq), pyromellitic dianhydride (37.2 g, 341.49 meq) and N-methylpyrrolidone (160 mL) were added to a reaction flask to
20 form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 23 hours. Epichlorohydrin (80.1 mL, 1025.28 meq) and triethylamine (1.42 mL) were added to the reaction mixture, and the reaction was continued at 65°C for 4 hours. Titration
25 in accordance with Example 5 indicated that 89.6% of the available carboxyl groups had reacted. Pyromellitic dianhydride (18.6 g, 170.75 meq), epichlorohydrin (40.0 mL, 512 meq) and triethylamine (0.71 mL) were added to the reaction mixture. The reaction was continued for 6
30 additional hours. Titration indicated that essentially all of the available carboxyl groups had reacted. A product weighing 266.9 g was recovered as in Example
35 1. The product had a surface tension of 15 dynes/cm as determined by the Zisman technique. Proton NMR confirmed the structural characteristics of the oligomeric

product.

EXAMPLE 8

Perfluoroalkylethanol (163.3 g, 342.3 meq), pyromellitic dianhydride (37.4 g, 343.33 meq) and N-methylpyrrolidone (168 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 21 hours. Epichlorohydrin (80.4 mL, 1029.12 meq) and triethylamine (1.43 mL) were then added to the reaction mixture. The reaction was then continued for 11.5 hours at 55°C. Titration in accordance with Example 5 indicated that 90.9% of the available carboxyls had reacted. Pyromellitic dianhydride (11.2 g, 102.82 meq), epichlorohydrin (24.1 mL, 308.48 meq) and triethylamine (0.43 mL) were then added to the reaction mixture. The reaction was continued for 10 additional hours at 55°C. Titration indicated that essentially no unreacted carboxyl groups remained. A product weighing 274.6 g was recovered as in Example 1. Proton MMR confirmed the structural characteristics of the oligomeric product mixture.

EXAMPLE 9

Perfluoroalkylethanol (161.9 g, 339.99 meq), pyromellitic dianhydride (37.1 g, 340.58 meq) and N-methylpyrrolidone (162 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 23 hours. Epichlorohydrin (79.8 mL, 1021.44 meq) and triethylamine (1.42 mL) were added to the reaction mixture, and the reaction was continued at 55°C for 10 hours. Titration in accordance with Example 5 indicated that 90% of the available carboxyl groups had reacted. Pyromellitic dianhydride (7.42 g, 68.12 meq), epichlorohydrin (16 mL, 204.8 meq) and triethylamine (0.28 mL) were added to the reaction mixture. The reaction was then continued for 10 additional hours at 55°C. Titration indicated that essentially all carboxyl groups had reacted. A product weighing 195.9 g was recovered as in Example 1. Proton NMR confirmed the structural characteristics of the oli-

gomer product mixture.

EXAMPLE 10

Perfluoroalkylethanol (160.0 g, 336.0 meq), pyromellitic dianhydride (35.6 g, 326.5 meq) and N-methylpyrrolidone (59 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 18.5 hours. Epichlorohydrin (78.8 mL, 1008.6 meq) and triethylamine (1.4 mL) were then added to the reaction mixture. The temperature of the reaction mixture was raised to 55°C, and the reaction mixture was allowed to react for 12 hours. Titration in accordance with Example 5 indicated that 90.8% of the carboxyls had been reacted. Pyromellitic dianhydride (14.2 g, 130.2 meq), epichlorohydrin (31.5 mL, 403.2 meq) and triethylamine (0.56 mL) were then added to the reaction mixture. The reaction was then continued for 9.5 additional hours at 55°C. Titration indicated that essentially no unreacted carboxyl groups remained. A product weighing 140 g was recovered as in Example 1. The product had a surface tension of 15 dynes/cm as determined by the Zisman technique. Proton NMR confirmed the structural characteristics of the oligomeric product.

COMPARATIVE EXAMPLE 11

Perfluoroalkylethanol (62.9 g, 132.09 meq), pyromellitic dianhydride (14.4 g, 132.19 meq) N-methylpyrrolidone (65 mL) and triethylamine (0.55 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 2 hours. Epichlorohydrin (30.99 mL, 396.67 meq) was then added to the reaction mixture. The temperature of the reaction mixture was raised to 75°C, and the reaction was allowed to continue for 5 hours. Titration indicated that essentially all of the available carboxyl groups had reacted. A product weighing 69.6 g was recovered as in Example 1 with some difficulty. The product had a surface tension of 12 dynes/cm as determined by the Zisman technique. The structure of

the single ring pyromellitate tetraester was confirmed by proton NMR. Thomas et al., copending commonly assigned Application Serial No. 350,544, disclosed that this material contained some materials of an oligomeric nature and that commercial preparations of this pyromellitate also contained some materials of an oligomeric nature.

EXAMPLE 12

Perfluoroalkylethanol (63.6 g, 133.56 meq), pyromellitic dianhydride (14.6 g, 134.03 meq), N-methylpyrrolidone (65 mL) and triethylamine (0.65 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and reacted for 2 hours. Epichlorohydrin (43.4 mL, 555.52 meq) was added to a reaction mixture, and the reaction mixture was reacted for 2 hours at 75°C. Pyromellitic dianhydride (7.3 g, 67.01 meq) was added and the reaction was continued at 75°C for an additional 5 hours. It was necessary to wash the product using a garing blender due to its soft consistency. A product weighing 70.3 g was obtained. The product had a surface tension of 8 dynes/cm as determined by the Zisman technique. Structural characteristics of the oligomeric product mixture were confirmed by proton NMR.

EXAMPLE 13

Perfluoroalkylethanol (157.1 g, 329.9 meq), pyromellitic dianhydride (34.7 g, 318.2 meq) and N-methylpyrrolidone (160 mL) were added to a reaction flask to form a reaction mixture. The reaction mixture was warmed to 45°C and allowed to react for 23 hours. Epichlorohydrin (112.1 mL, 1434.88 meq), pyromellitic dianhydride (17.4 g, 159.6 meq) and triethylamine (2.0 mL) were then added to the reaction mixture. The temperature of the reaction mixture was raised to 65°C, and the reaction mixture was allowed to react for 7 hours. Titration in accordance with Example 5 indicated that 99.1% of the available carboxyl moieties had reacted. A product weighing 253.0 g was recovered as in Example

1. The product had a surface tension of 14 dynes/cm as determined by the Zisman technique. Proton NMR confirmed the structural characteristics of the oligomeric product.

EXAMPLE 14

Performance Evaluation

5 Solutions were prepared from the products of Examples 1-13 of 0.25g of each product in 100 mL acetone. It will be appreciated that the products of Examples 1-10 and 12-13 are oligomeric mixtures and that the product of Example 11 is a pyromellitate having a structure similar to the pyromellitates of Mares et al., Oxenrider et al., and Oxenrider as described in the Background section of this application. Therefore, Example 11 is a comparative example, and it is labeled as C-11 in Tables I-IV. Swatches of polyamide and polyester fabrics were dipped in the solutions, air dried for 1 to 3 hours, and then annealed for 30 minutes in a circulating oven at a selected temperature. These swatches were then tested for oil repellency by the procedures of AATC Test No. 118-1966 initially and after being subjected to a number of laundry cycles.

15 Tables I, II, and III illustrate the oil repellency imparted to Nylon 6, Nylon 6,6 and poly(ethylene terephthalate) fibers when the compositions produced by Examples 1-13 were applied to said fibers as described hereinabove. Table IV is a summary of the number of laundry cycles in which said fibers having applied thereto the compositions of Examples 1-13 retained an oil repellency of at least 4.

TABLE I

0095036

Fiber		Nylon 6							
Anneal Temp.		100°C							
Example		1	2	3	4	5	6	7	8
5	Laundry Cycles								
	0	7	7	6	6	7	6	6	7
	1	6	7	6	6	6	6	6	7
	2	6	7	6	6	6	6	6	6
	3	6	6	6	6	6	6	6	6
10	4	6	6	5	6	6	6	6	6
	5	5	6	5	5	6	6	5	6
	6	5	6	5	5	5	5	5	6
	7	5	6	5	4	5	5	5	5
	8	5	5	4	4	4	5	5	5
15	9	4	5	4	3	4	4	4	4
	10	2	4	3		4	4	4	3
	11		4			3	3	3	
	12		4						
	13		4						
20	14		3						

TABLE I (CONTINUED)

Example		9	10	C-11	12	13
	Laundry Cycles					
	0	7	7	7	7	7
25	1	7	6	6	7	6
	2	7	6	6	6	6
	3	6	6	6	6	6
	4	6	5	6	6	5
	5	6	5	6	5	5
30	6	6	5	6	5	4
	7	6	4	3	5	4
	8	6	4		5	3
	9	5	4		4	
	10	5	3		3	
35	11	4				
	12	2				
	13					
	14					

TABLE II

Fiber		Nylon 6,6							
Anneal Temp.		120°C							
Example		1	2	3	4	5	6	7	8
5	Laundry Cycles								
	0	6	6	6	6	6	6	6	7
	1	6	6	6	6	6	6	6	6
	2	6	6	6	6	6	6	6	6
	3	6	6	6	6	6	6	6	6
10	4	6	6	6	6	6	6	6	6
	5	5	5	5	5	5	6	6	5
	6	5	5	5	5	5	5	5	5
	7	5	5	5	4	5	5	4	5
	8	4	5	4	4	4	4	4	5
15	9	3	3	4	4	4	4	4	5
	10			4	4	2	4	3	4
	11			3	3		3		3
	12								

TABLE II (CONTINUED)

Example	9	10	C-11	12	13
20	Laundry Cycles				
	0	7	6	6	6
	1	7	6	6	6
	2	6	6	6	6
25	3	6	6	6	5
	4	6	5	5	4
	5	5	4	4	5
	6	5	4	4	5
	7	4	4	2	5
30	8	4	4		4
	9	3	3		4
	10				4
	11				4
	12				3
35					

TABLE III

0095036

Fiber		Poly(ethylene terephthalate)							
Anneal Temp.		140°C							
Example		1	2	3	4	5	6	7	8
5	Laundry Cycles								
	0	6	6	6	6	6	6	6	7
	1	6	6	6	6	6	6	6	6
	2	6	6	6	6	6	6	6	6
	3	6	6	5	5	6	6	6	6
10	4	6	6	5	5	6	5	5	6
	5	6	5	5	5	5	5	5	6
	6	5	5	5	5	5	5	5	6
	7	5	5	5	5	5	5	5	5
	8	5	5	5	5	5	5	5	5
15	9	5	5	5	5	4	5	4	5
	10	5	5	4	4	4	5	4	4
	11	4	5	4	4	4	4	4	4
	12	4	4	4	4	4	4	4	4
	13	4	4	4	4	4	4	4	4
20	14	4	4	4	4	4	4	3	4
	15	4	4	3	3	4	4		3
	16	4	3			3	3		
	17	4							
	18	4							
25	19	4							
	20	4							
	21	3							

30

35

TABLE III (CONTINUED)

0095036

Example	9	10	C-11	12	13
Laundry Cycles					
	0	7	6	7	6
5	1	7	6	6	6
	2	6	6	6	6
	3	6	6	6	5
	4	6	5	6	5
	5	6	5	6	5
10	6	6	5	6	5
	7	5	5	6	5
	8	5	5	5	5
	9	5	5	5	5
	10	5	5	4	4
15	11	5	5	4	4
	12	4	4	4	4
	13	4	4	3	4
	14	4	3		4
	15	4			4
20	16	3			4
	17				3
	18				
	19				
	20				
25	21				

30

35

TABLE IV

Example		<u>Nylon 6 Swatches</u>				<u>Nylon 6,6 Swatches</u>		
		100°C	120°C	140°C	155°C	100°C	120°C	140°C
5	1	9	10	7	7	9	8	11
	2	13	12	7	6	8	8	11
	3	9	9	7	6	10	10	11
	4	8	9	6	6	10	10	11
	5	10	9	6	6	8	9	9
10	6	10	9	6	5	8	10	10
	7	10	9	6	6	7	9	10
	8	9	9	6	8	10	10	10
	9	11	11	10	8	9	8	9
	10	9	8	4	4	6	8	7
15	C-11	6	9	9	8	5	6	8
	12	9	9	8	8	10	11	12
	13	7	7	6	5	6	6	6
Example		<u>Nylon 6,6 Swatches</u>			<u>PET Swatches</u>			
		155°C			100°C	120°C	140°C	155°C
20	1	13			12	12	20	21
	2	11			11	11	15	16
	3	9			12	15	14	13
	4	10			11	8	14	12
	5	9			15	16	15	16
	6	10			13	14	15	14
25	7	7			14	11	13	12
	8	10			12	14	14	15
	9	9			13	14	15	15
	10	6			14	13	13	14
30	C-11	10			9	10	12	12
	12	12			15	16	16	15
	13	4			7	9	9	9

The results of Example 14 as illustrated by Tables I-IV indicate that the oligomeric mixtures prepared by the first mode of this invention are highly effective surface modifiers. An oil repellency of 4 after 7 laundry cycles is generally considered a most satisfactory rating. Table IV illustrates that the oligomers of

this invention retained an oil repellency of 4 after 7 laundry cycles in most cases. Furthermore, the oligomeric mixtures out performed the comparative pyromellitate monomers of Example 11 in most instances, except for the oligomers produced by Example 13 which employed a slightly modified synthetic procedure.

Example 15

Low Temperature Annealing Performance Evaluation

Utilizing the procedures employed in Example 14, fibers treated with the products of Examples 6, 7, and 11 were annealed at temperatures from 50°C to 90°C and then tested for oil repellency. As in Example 14, the product of Example 11 was used for comparative purposes. The results are illustrated in Table XIII.

TABLE V

Fibers Anneal Temp. Example	Nylon 6 50°C 6 7 C-11	Nylon 6 60°C 6 7 C-11	Nylon 6 70°C 6 7 C-11	Nylon 6 90°C 6 7 C-11
Laundry Cycles				
0	7 7 7	7 7 7	7 7 7	7 7 7
1	6 6 4	6 6 4	6 6 6	6 6 5
2 6	6 2 6	6 2 6	6 2 6	6 2
3	5 6	6 6	6 6	6 6
4	5 6	5 6	6 6	6 6
5	4 6	5 5	5 6	6 6
6	4 5	5 5	5 5	5 5
7	4 5	4 5	4 5	4 5
8	3 4	3 4	4 4	4 4
9	4	4	4 4	4 4
10	3	2	3 2	3 3

The above results in Table V clearly illustrate that fibers treated with the oligomeric mixtures prepared via the first mode of this invention which are annealed at low temperatures will have desirable soil resistance properties. On the other hand, Table V indicates that fibers treated with the pyromellitate

monomer of comparative Example 11 did not achieve a satisfactory oil repellency rating when said fibers were annealed at low temperatures.

EXAMPLES 16-30

5 A 500 mL 3-necked round bottom flask was fitted with stirring bar, thermometer, water condenser, nitrogen inlet and vent. All glassware was air dried at 120°C and cooled in a dessicator. In each example, an amount of telomer fluorinated alcohols of the formula
 10 $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with $n = 2, 3, 4$ and 5 having 2.1 meq OH/g was charged and weighed. Thereafter weighed amounts of pyromellitic dianhydride (PMDA) and N-methylpyrrolidone (NMP) were added and the mixture heated for at least 10 hours at 45°C. Thereafter epi-
 15 chlorohydrin in excess and triethylamine (TEA) at 3 mol % of carboxyl were added. The reaction mixture was then kept at 55-58°C for a period (10-15 hours) while the free COOH was monitored by titration with alcoholic KOH. On completion, the reaction mixture was poured
 20 into 15-20 volumes of agitated cold water in an ice bath, stirred, the water siphoned off and replaced, stirred and the water replaced. The product was washed at least three times, filtered and dried overnight at room temperature under vacuum.

EXAMPLE 16

The above preparation was conducted with the following quantities:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
30 Fluoroalcohols	174.5	366.45	366.45
PMDA	43.2	396.3	198.17
NMP	399.5 (178 mL)	-	-
Epichlorohydrin	101.7 (86.0 mL)	1099.87	1099.87
TEA	1.12 (1.53 mL)	11.02	11.02

35 The product after the above work-up was 198.0 g of cream colored, slightly tacky solids.

EXAMPLE 17

The above procedure was followed for the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	163.2	342.72	342.72
PMDA	62.3	571.2	285.6
NMP	(160 mL)	-	-
5 Epichlorohydrin	158.5 (134 mL)	1713.7	1713.7
TEA	1.73 (2.38 mL)	17.09	17.09

The product after a similar work-up was 266.0 g of brown two-tone slightly tacky solids. A portion (16.4 g) was used for analysis and testing in organic sol-
 10 vents, the balance reserved for testing in aqueous emul-
 sions.

EXAMPLE 18

The above procedure was followed for the following recipe, except that the alcohol was charged after the
 15 mixture of pyromellitic dianhydride and N-methylpyrrolidone was heated to 45°C.

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	145.2	304.92	304.92
PMDA	66.5	609.84	304.92
20 NMP	(143 mL)	-	-
Epichlorohydrin	169.23 (143.1 mL)	1830.13	1830.13
TEA	1.692 (2.32 mL)	16.72	16.72

The final reaction product was refrigerated overnight before pouring into 3.5 L water and washing.
 25 After vacuum drying, 264.7 g tan solids were recovered, with 248.7 g reserved for emulsion testing and 16.0 g, for analysis and testing in acetone solution.

EXAMPLE 19

The above procedure was followed for the following
 30 recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	206.2	433.02	433.02
PMDA	55.5	509.17	254.59
NMP	(178 mL)	-	-
35 Epichlorohydrin	120.19 (101.6 mL)	1299.38	1299.38
TEA	1.3 (1.80 mL)	12.97	12.97

The final reaction mixture was refrigerated overnight, and, in two portions, it was poured into 3 L

stirred ice-cold water surrounded by an ice bath. After washing with cold water several times (cooling and blending in a Waring blender several times), the product was recovered by filtration and vacuum dried to produce
 5 266.8 g of tacky light brown solids.

EXAMPLE 20

The above procedure was repeated using the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
10 Fluoroalcohols	170.5	358.05	358.05
PMDA	55.8	511.93	255.96
NMP	(150 mL)	-	-
Epichlorohydrin	99.37 (84 mL)	1074.29	1074.29
TEA	1.09 (1.49 mL)	10.73	10.73

15 In this Example, the epichlorohydrin amount was measured to be three times the fluoroalcohol rather than three times the carboxyl.

The product after a similar work-up was 260.9 g of dark brown tacky solids. A small amount (10-12 g) was
 20 used for testing in acetone solution, with the balance reserved for emulsion testing.

EXAMPLE 21

The above procedure was repeated using the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
25 Fluoroalcohols	25.2	52.92	52.92
PMDA	6.78	62.20	31.10
NMP	- (24 mL)	-	-
Epichlorohydrin	14.69 (12.42 mL)	158.84	158.84
30 TEA	0.16 (0.22 mL)	1.58	1.58

Again, the epichlorohydrin was computed as three times the fluoroalcohol. After a similar work-up, the product recovered was 24.6 g of slightly tacky solids, mostly tan with some cream colored particles.

EXAMPLE 22

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The above procedure was repeated using the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
5 Fluoroalcohols	18.0	37.8	37.8
PMDA	10.3	94.5	47.25
NMP	- (30 mL)	-	-
Epichlorohydrin	26.22 (22.2 mL)	283.5	1099.87
TEA	1.12 (1.53 mL)	11.02	11.02
10 After a similar work-up, the product recovered was 32.7 g of tan solids.			

EXAMPLE 23

The above procedure was followed using the following recipe in an attempt to employ a 1:1.67 fluoro-alcohol pyromellitic dianhydride ratio:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	18.1	38.01	38.01
PMDA	13.8	126.7	63.35
NMP	- (30 mL)	-	-
20 Epichlorohydrin	35.16 (29.7 mL)	380.1	380.1
TEA	0.38 (0.53 mL)	3.8	3.8

Five hours after addition of triethylamine and epichlorohydrin, an attempt to remove the first aliquot for titration with alcoholic KOH failed because the reaction mixture had formed a rubbery gel insoluble in N-methylpyrrolidone.

EXAMPLE 24

The above procedure was followed, with the following modifications for ethyl acetate as solvent, based in part upon the process of U.S. Patent 4,252,982 (December 1981):

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	28.2	59.22	59.22
PMDA	8.6	78.96	39.48
35 NMP	- (30 mL)	-	-
Epichlorohydrin	21.9 (18.5 mL)	236.88	236.88
TEA	0.24 (0.33 mL)	2.37	2.37

After epichlorohydrin and triethylamine addition, an

additional 10 mL ethyl acetate was added. Twenty-four hours after epichlorohydrin and trimethylamine addition, with titration showing 97.2% carboxyl conversion, the reaction mixture was cooled, poured into 1.3 L stirred ice cold water and washed four times. After vacuum drying, 33.3 g of cream colored, very slightly tacky solids were recovered. A similar product could have been produced by vacuum drying the reaction mixture and washing the residue.

EXAMPLE 25

The above procedure was followed, with the following modifications for methyl isobutyl ketone as solvent:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
Fluoroalcohols	28.0	58.8	58.8
PMDA	8.5	78.4	39.2
NMP	- (30 mL)	-	-
Epichlorohydrin	21.8 (18.4 mL)	235.5	235.5
TEA	0.24 (0.33 mL)	2.35	2.35

Because the initial reaction mixture had solid present, an additional 10 mL methyl isobutyl ketone was added and the temperature was raised from 45°C to 55°C. Solids remained, but the reaction was continued by adding epichlorohydrin and triethylamine. After 16 hours at 55°C, the reaction mixture showed 97.6% carboxyl conversion. It was poured into 1.4 L stirred iced water to form a paste (methyl isobutyl ketone is water-insoluble). The water was siphoned off and the paste dissolved in chloroform. The solution was then washed three times with water, filtered and then dried with magnesium sulfate. After flash evaporation, 25.0 g of tacky light amber solids were recovered.

EXAMPLE 26

The above procedure was followed, except a 98% pure alcohol $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$ (MW 464) was used in place of the fluoroalcohol mixture in the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
1,1,2,2-tetrahydro-			
perfluorodecanol	20.0	43.1	43.1
PMDA	6.26	57.47	23.74
5 NMP	- (20 mL)	-	-
Epichlorohydrin	<u>18.93</u> (16.0 mL)	<u>204.6</u>	<u>204.6</u>
TEA	0.17 (0.24 mL)	1.72	1.72

After the normal work-up, 21.0 g of off-white solids were recovered. This product was used for proton and carbon 13 NMR, mass spectroscopy and other techniques for structural analysis, as well as for laundry testing.

EXAMPLE 27

The above procedure was followed, using the 98% pure fluoroalcohol of Example 11, in the following recipe:

	<u>g</u>	<u>meq</u>	<u>mmol</u>
1,1,2,2-tetrahydro-			
perfluorodecanol	18.42	39.70	19.35
PMDA	6.18	56.71	28.35
20 NMP	- (26 mL)	-	-
Epichlorohydrin	15.74 (13.3 mL)	170.13	170.13
TEA	0.17 (0.24 mL)	1.70	1.70

The product, after the usual work-up, was 22.7 of cream-colored solids.

EXAMPLES 28-30

The samples (Examples 28, 29 and 30) were prepared by mixing equal weights of the monomer of Mares et al. prepared in N-methylpyrrolidone as in U.S. Patent 4,321,403 to Oxenrider et al. and the product of Examples 17, 18 and 20, respectively. It will be appreciated that the products of Examples 2, 3 and 5 had fluoroalcohol/pyromellitic dianhydride ratios of 1:0.83, 1:1.0 and 1:0.71 and thus had relatively high proportions of oligomeric products. After mixing with monomer, the products had overall fluoroalcohol/pyromellitic dianhydride ratios in the 1:0.6 - 1:0.75 range but are likely to have more higher oligomers than materials (e.g. Example 23) prepared with initial ratios at this level.

EXAMPLE 31

Performance Evaluation

Solutions were prepared from the products of Examples 16-30 and the reference monomeric material of 0.25 g of each product in 100 mL acetone. Swatches of nylon 6, nylon 6,6 and poly(ethylene terephthalate) fibers were dipped in the solutions, hand pressed between aluminum foil and plate, air dried for 1 to 3 hours and then annealed for 30 minutes at one or more selected temperatures (100°C, 120°C, 140°C or 155°C). A plurality of each sample was then tested and rated for oil repellency initially, and after a selected number of laundry cycles (generally up to 10 or 11 or until the rating fell below 4) by the procedures of AATC Test No. 118-1966.

The results of Example 31 are summarized in Tables VI and VII which illustrate the number of laundry cycles over which each run (for a specific product and annealing temperature) retained an oil repellency value of at least 4. Next to each Example number is the fluoro-alcohol/pyromellitic dianhydride ratio used for the first step of the product synthesis:

TABLE VI

Example	Ratio	Nylon 6 Swatches				PET Swatches	
		100°C	120°C	140°C	155°C	140°C	155°C
5	16	1:0.54	2	4	6	7	9
	17	1:0.83	6	3	4	3	4
	18	1:1.0	1	4	2	2	3
	19	1:0.59	6	8	7	6	10
	20	1:0.71	7	9	7	7	10
10	21	1:0.59	4	7	8	5	11
	22	1:1.24	1	2	2	1	2
	23	1:1.67	gelled				
	24	1:0.67	3	12	10	9	12
	25	1:0.67	7	9	8	7	11
15	26	1:0.67	7	14	8	7	19
	27	1:0.71	6	8	8	7	19
	28	* 9	11	8	6	13	15
	29	* 10	10	8	7	13	13
	30	* 8	10	10	7	13	20
Comp.	1:0.50	4	7	6	6	11	11

*achieved by blending 17, 18 and 20 with equal weights of the comparative material.

The results in Table VI show improved retention, especially on nylon 6 at the low (100°C and 120°C) annealing temperatures, for the products of Examples 19-21 and 24-30.

The results with nylon 66 cloth are more limited, and are summarized in Table VII below by the number of laundry cycles over which an oil repellency rating of at least 4 was obtained:

TABLE VII

Example	Ratio	100°C.	120°C.	140°C.	155°C.
18	1:1.0	3	3	3	3
19	1:0.59	6	8	7	7
5 22	1:1.25	1	1	1	2
24	1:0.67	6	6	6	12
25	1:0.67	5	7	6	7
26	1:0.67	7	7	10	14
27	1:0.71	5	5	9	11
10 28	*	9	10	11	10
29	*	9	10	10	12
30	*	9	9	13	13
Comp.	1:0.5	3	7	6	6

* obtained by blending 17, 18 and 20 with
equal weights of comparative material.

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WE CLAIM:

1. A process for the production of an organic mixture useful as a fiber surface modifying agent by reaction of pyromellitic dianhydride, fluorinated alcohol
5 and an oxirane compound selected from the group consisting of epichlorohydrin, epibromohydrin, and propylene oxide, characterized by the organic mixture containing more than one mole of groups derived from pyromellitic dianhydride per two moles of groups derived from fluorinated alcohol, and being either a first process of:
10

(a) reacting pyromellitic dianhydride with fluorinated alcohol at a mole ratio of two moles of fluorinated alcohol per mole pyromellitic dianhydride to produce a pyromellitate having two fluorinated ester
15 moieties and two carboxylic acid moieties; and

(b) reacting said pyromellitate of step (a) with an excess of oxirane compound in the presence of additional pyromellitic dianhydride to produce said organic mixture comprising oligomeric compounds; wherein said
20 oxirane compound reacts with said carboxylic acid moieties to produce an ester having a primary or secondary alcohol, and wherein said alcohol reacts with said additional pyromellitic dianhydride to produce ester-linking moieties and carboxylic acid moieties capable of reacting
25 with said oxirane compound to produce additional esters having primary or secondary alcohols; or a second process of:

(a') reacting pyromellitic dianhydride with fluorinated alcohol at a mole ratio of fluorinated alcohol to pyromellitic dianhydride between 1:0.55 and 1:1.0 to
30 form a partially esterified pyromellitate having fluorinated ester groups, free acid groups and anhydride groups; and

(b') reacting the partially esterified product with oxirane compound in an amount sufficient to cause
35 essentially all of the free acid groups and anhydride groups to be esterified.

2. The process of claim 1 wherein said fluorinated

alcohol is of the formula: $\text{CF}_3(\text{CF}_2)_p\text{R}'\text{OH}$ wherein R' is alkylene of 2 to 6 carbons and p is an integer of 3 to 15.

3. The process of claim 2 wherein said fluorinated alcohol is a mixture of compounds of the formula $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with n being from 1 to 6.

4. The process of any previous claim conducted in an aliphatic ester solvent having a boiling point less than 150°C .

5. The process of any of claims 1 to 3 conducted in a solvent consisting essentially of N-methylpyrrolidone.

6. A process according to any previous claim wherein said excess pyromellitic dianhydride is added to a reaction medium in said step (b) when 50% to 100% of the carboxylic acid moieties have been esterified.

7. A process according to claim 6 wherein said excess pyromellitic dianhydride is added to a reaction medium in said step (b) when 85% to 95% of the carboxylic acid moieties have been esterified.

8. The process of any of claims 1 to 5 wherein said mole ratio of said step (a') is between 1:0.6 and 1:0.85.

9. The process of claim 8 wherein said mole ratio of said step (a') is between 1:0.65 and 1:0.75.

10. The process of any previous claim wherein said oxirane compound is epichlorohydrin.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	US-A-3 994 951 (S.R. SANDLER) * Column 1, line 29 - column 2, line 60 * -----	1	C 07 C 69/76 C 07 C 67/26 D 06 M 13/20
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 07 C 69/00 C 07 C 67/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-06-1983	Examiner KINZINGER J.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	