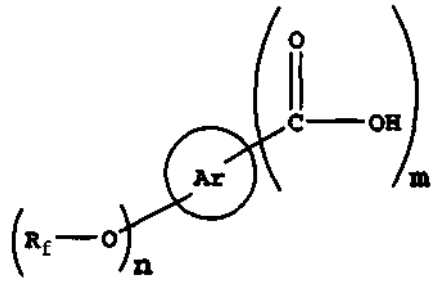
# PROCESS FOR THE SYNTHESIS OF FLUORINATED ETHERS OF AROMATIC ACIDS

## Abstract of the Invention

Fluorinated ethers of aromatic acids are produced from halogenated aromatic acids in a reaction mixture containing a copper (I) or copper (II) source and a diamine ligand that coordinates to copper. The fluorinated ethers of aromatic acids made using the process described herein can be applied to, e.g., fibers, yarns, carpets, garments, films, molded parts, paper and cardboard, stone, and tile to impart soil, water and oil resistance. By incorporating the fluorinated ethers of aromatic acids, or diesters thereof, into polymer backbones, more lasting soil, water and oil resistance, as well as improved flame retardance, can be achieved.

WE CLAIM :

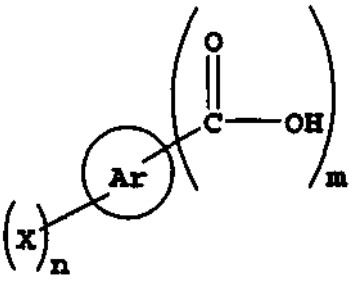
1. A process for preparing a fluorinated ether of an aromatic acid, the ether being 'represented by the structure of the following Formula I



I

wherein Ar is a $C_6$~$C_{2o}$ monocyclic or polycyclic aromatic nucleus, n and m are each independently a nonzero value, n+m is less than or equal to 8, and wherein $R_f$ is a fluorinated alkyl, alkaryl, aralkyl or aryl group, optionally containing one or more ether linkages -0- , with the proviso that $R_f$ is not attached to the ether oxygen in Formula I via a $CF_2$ group or a $CF_2CH_2CH_2$ group, comprising:

(a) contacting a halogenated aromatic acid that is represented by the structure of the following Formula II:




II

wherein each X is independently C1, Br or I, and Ar, n and m are as set forth above, with

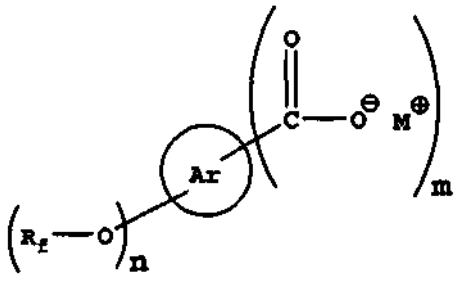
(i) a total of from about n+m to about n+m+1 equivalents of the alcoholate $R_fO^-M^+$ (wherein M is Na or K) per equivalent of halogenated aromatic acid, in a polar aprotic solvent or in $R_fOH$ as a solvent;

(ii) a copper (I) or copper (II) source; and

(iii) a diamine ligand that coordinates to copper,

to form a reaction mixture;

(b) heating the reaction mixture to form the m-basic salt of the product of step (a), as represented by the structure of the following Formula III;



III

(c) optionally, separating the Formula III m-basic salt from the reaction mixture in which it is formed; and

(d) contacting the Formula III m-basic salt with acid to form therefrom a fluorinated ether of an aromatic acid.

2. A process according to Claim 1 wherein $R_f$ is selected from the group consisting of:

(a) $CF_3(CF_2)_a(CH_2)b$ - , wherein a = an integer from 0 to 15 and b = 1, 3 or 4;

(b) $HCF_2(CF_2)_c(CH_2)_d$-, wherein c = an integer from 0 to 15 and d = 1, 3, or 4;

(c) $CF_3CF_2CF_2OCFHCF_2(OCH_2CH_2)_e$ - and $CF_3CF_2CF_2OCF_2CF_2(OCH_2CH_2)_e$ -, wherein e = an integer from 1 to 12;

(d) $(CF_3)_2CH$- ,

(e) $(CF_3CF_2CFH)(F)(CF_3)C$- ,

(f) $(CF_3CF_2CFH)(F)(CF_3)CCH_2$- ,

(g) $(CF_3)_2(H)C(CF_3CF_2)(F)C$ - ,

(h) $(CF_3)2(H)C(CF_3CF_2)$ $(F)CCH_2$- ; and

(i) pentafluorophenyl.

3. A process according to Claim 1 wherein the halogenated aromatic acid is selected from the group consisting of 2-bromobenzoic acid, 2,5-dibromobenzoic acid, 2-bromo-5-nitrobenzoic acid, 2-bromo-5-methylbenzoic acid, 2-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2-chloro-3,5-dinitrobenzoic acid, 2-chloro-5-methylbenzoic acid, 2-bromo-5-methoxybenzoic acid, 5-bromo-2-chlorobenzoic acid, 2,3-dichlorobenzoic acid, 2-chloro-4-nitrobenzoic acid, 2,5-dichloroterephthalic acid, 2-chloro-5-nitrobenzoic acid, 2,5-dibromoterephthalic acid, and 2,5-dichloroterephthalic acid.

4. A process according to Claim 1 wherein, in step (a), a total of about n+m to n+m+1 normal equivalents of $RfO"M^+$ are added to the reaction mixture per equivalent of the halogenated aromatic acid.

5. A process according to Claim 1 wherein the copper source comprises a Cu(I) salt, a Cu(II) salt, or a mixture thereof.

6. A process according to Claim 5 wherein the copper source is selected from the group consisting of CuCl, CuBr, Cul, $Cu_2S0_4$, $CuN0_3$, $CuCl_2$, $CuBr_2$, $CuI_2$, $CuS0_4$, $Cu(N0_3)_2$, and mixtures thereof.

7. A process according to Claim 1 wherein the ligand comprises a cyclohexyl diamine.

8. A process according to Claim 1 where the ligand comprises an N,N'-substituted diamine.

9. A process according to Claim 1 wherein copper is provided in an amount of between about 0.1 and about 5 mol% based on moles of halogenated aromatic acid.

10. A process according to Claim 1 wherein the ligand is provided in an amount of between about one and about two molar equivalents per mole of copper.

11. A process according to Claim 1 further comprising a step of subjecting the ether of the aromatic acid to a reaction to prepare therefrom a compound, monomer, oligomer or polymer.

12. A process according to Claim 11 wherein a polymer prepared comprises at least one member of the group consisting of pyridobisimidazole, pyridobisthiazole, pyridobisoxazole, benzobisimidazole, benzobisthiazole, and benzobisoxazole moieties.

13. A process according to Claim 12 wherein a polymer prepared comprises a fluorinated pyridobisimidazole-2,6-diyl(2,5-dialkoxy-p-phenylene)

polymer or a fluorinated pyridobisimidazole-2,6-diyl(2,5-diareneoxy-p-phenylene)polymer.

14. An article comprising a composition made by a process according to Claim 1.

15. An article comprising a composition made by a process according to Claim 11.

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