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3,645,990

## FLUORINATED OIL- AND WATER-REPELLENT AND DRY SOIL RESISTANT POLYMERS

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8 Claims

### ABSTRACT OF THE DISCLOSURE

Fluorinated oil- and water-repellent and dry soil resistant aqueous emulsion polymers containing units derived from monomers having the structure



wherein  $R_f$  is a perfluoroalkyl group of about 4 through 14 carbon atoms, and methyl acrylate or ethyl acrylate, and optionally containing small amounts of units derived from monomers selected from  $CH_2=CRCONHCH_2OH$ ,  $CH=CRCO_2CH_2CH_2OH$  and mixtures thereof wherein R is H or  $CH_3$ .

### BACKGROUND OF THE INVENTION

#### (1) Field of the invention

The invention relates to novel fluorinated aqueous emulsion polymers containing



and methylacrylate or ethyl acrylate wherein  $R_f$  is a perfluoroalkyl group of from about 4–14 carbon atoms, which are useful in treating textile fabrics to render said fabrics oil- and water-repellent and dry soil resistant.

#### (2) Description of the prior art

While a variety of art-known fluorine containing polymeric materials presently used in the treatment of textile fabrics are capable of effecting oil and water repellency in said fabrics, there are still several extant problems in the area of repellency which are not overcome by known oil- and water-repellent fluorinated polymers.

One such problem is that most, if not all, of the presently known fluorinated oil- and water-repellent polymer systems require a rather high temperature cure after application to develop oil repellency. This is completely incompatible with most permanent press systems. The resins used in such systems also require rather high temperature cures but such cure cannot be applied until after the textile is converted into the final form of the garment and the desired creases applied. Textiles treated with permanent press resins and presently available oil- and water-repellents are therefore not oil-repellent until the garment is complete. A large amount of such textile is soiled by oils and greases during garment manufacture without any benefit being gained from the oil- and water-repellent. The textile and garment manufacturers would, of course, like to have their permanent press treated fabric oil-repellent during garment manufacture but presently they cannot.

Another problem is that fluorinated polymers which provide repellency to oils and water (liquids) do not by necessity have any repellency for dry-soils, i.e., particulate matter. Such particulate matter usually soils a fabric by being rubbed or ground into the fabric, for example, between and among the individual threads. Removal of such dry-soil requires the laundering medium to suspend the particle and float it away from the fibers of the fabric. If the fabric repels water, of course, it is more difficult to remove the particulate matter.

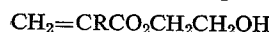
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Novel fluorinated aqueous emulsion polymers have now been discovered which, when used in treating textile fabrics, display the desired properties and quantities such as imparting oil repellency prior to curing and also imparting to the treated textile fabric a resistance to dry soiling, thus overcoming some of the outstanding problems in the area of oil and water repellency and dry soil resistance which exist for garment manufacturers and the like.

### SUMMARY OF THE INVENTION

The present invention is directed to oil- and water-repellent and dry soil resistant aqueous emulsion polymers. These polymers contain about 70 to 95 parts of units derived from monomers having the structure  $R_fCH_2CH_2O_2CC(CH_3)=CH_2$  where  $R_f$  is a perfluoroalkyl group of about  $C_{4-14}$ , and about 30 to 5 parts of units derived from methyl acrylate or ethyl acrylate monomers. The sum of these monomer-derived units present in the polymer is 100 parts.

It is also often desirable to add a monomer selected from units derived from



and mixtures thereof, wherein R is H or  $CH_3$ . The amount of units derived from these monomers which will be used may vary from 0 to 1 part per 100 parts of the other two monomers.

### DESCRIPTION OF THE INVENTION

These new fluorinated polymers contain two essential ingredients. The first is a monomer having the structure  $R_fCH_2CH_2O_2CC(CH_3)=CH_2$  wherein  $R_f$  is a perfluoroalkyl group of from about 4 to 14 carbons. From about 70 to 95 parts of units derived from such monomers must be present in the polymer.

In these monomers  $R_fCH_2CH_2O_2CC(CH_3)=CH_2$ , the perfluoroalkyl group  $R_f$  is preferably a mixture of straight chain groups  $CF_3CF_2(CF_2)_n-$  where n is 4, 6, 8, 10 and 12 in the approximate weight ratio 35/30/18/8/3, the monomer having an average molecular weight of 522. These are preferred since mixtures of these groups are commercially available, financially practical and give the best results. Branched or other straight chain perfluoroalkyl groups may, however, also be utilized.

The second essential monomer in the present polymers is methyl acrylate or ethyl acrylate with methyl acrylate being preferred. From about 30 to 5 parts of units derived from such monomers must be present in the polymer.

The sum of the units derived from the first and second essential monomers present in the polymer is 100 parts.

It is often desirable though not essential to include in the polymers of this invention small amounts of units derived from certain monomers which can lead to greater durability to dry-cleaning and laundering. While satisfactory durability exists absent these monomers, a still more durable product may result when they are present. These monomers are chosen from N-hydroxyalkyl acrylamides of structure  $CH_2=CRCONHCH_2OH$ , hydroxyalkyl acrylic esters of structure  $CH_2=CRCO_2CH_2CH_2OH$  and mixtures thereof, wherein R is H or  $CH_3$ . The monomers which are used and are commercially available are N-methylol acrylamide, N-methylol methacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and of these, N-methylol acrylamide and 2-hydroxyethyl methacrylate are preferred. About 0 to 1 part of units derived from these optional monomers may be present per 100 parts of units derived from the two essential monomers.

The preferred polymers of this invention contain about 85 parts  $R_fCH_2CH_2O_2CC(CH_3)=CH_2$ , 15 parts methyl acrylate, 0.25 part N-methylol acrylamide and 0.25 part

2-hydroxyethyl methacrylate. The polymers of this invention are aqueous emulsion polymers, that is, prepared by an aqueous emulsion polymerization technique.

In preparing the polymers of this invention according to the usual emulsion polymerization techniques, it is preferable to control the molecular weight of the polymer by addition of small amounts of a chain transfer such as dodecylmercaptan. In general, from about 0.04% to 1.0%, based on total weight of monomers, is used. The polymers having lower molecular weight, i.e., those resulting when the amount of dodecylmercaptan is nearer 1.0%, generally have somewhat better soil resistance than the polymers of higher molecular weight, i.e., those resulting when the amount of dodecylmercaptan is nearer 0.04% or is entirely absent.

The emulsion polymerization is otherwise quite standard. The monomers are preemulsified in water using a suitable emulsifying agent, the initiator is added, polymerization is initiated by heating and heating is continued until polymerization is complete. Any emulsifying agent which does not interfere with polymerization may be used. Preferably, cationic agents such as either the quaternary salts  $[R'N(CH_3)_3]^+X^-$  or the acid salts  $[R'N(CH_3)_2 \cdot HX]$  are used. In both cases  $R'$  is a longer chain alkyl group, of from about 12 to 20 carbons, and  $X$  is a water solubilizing cation such as halide ion, acetate ion, etc. Any water soluble initiator may be used; the water soluble azo compounds such as azobis(isobutyramidine)dihydrochloride are preferred.

The polymers of this invention are generally applied to textiles as aqueous emulsions by spraying, dipping, padding or other well-known methods. After excess liquid has been removed, for example, by squeeze rolls, the treated fabric is dried, then cured by heating, e.g., at 275° to 380° F. for at least 40 seconds. As will be seen in Example 3, it is not necessary to cure the treated fabrics to obtain oil repellency as such develops on merely drying. The curing does, however, increase durability and hence is desirable.

The unusual ability of the polymers of this invention to develop oil repellency merely on air drying and even to a degree while wet is of great value since it gives to the textiles some protection from soiling even during processing. The oil repellency is markedly increased by curing as will be seen in Example 2.

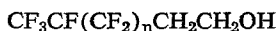
The polymers of this invention can be coapplied with other adjuvants such as textile resins, water-repellents and other additives often added to textiles if so desired. Such other additives which detract from dry soil resistance, however, should be avoided when maximum soil resistance is desired.

Dry soil resistance is particularly important on textiles coming in contact with dirt and rubbing action such as upholstery of all kinds. A particularly important use for the polymers of this invention is on automobile upholstery, particularly the nylon tricot variety.

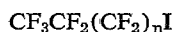
### EXAMPLES

The following examples are intended to be merely illustrative of the invention and not in limitation thereof. Unless otherwise indicated, all quantities are by weight.

The fluorinated monomer in all cases had the structure  $CF_3CF_2(CF_2)_nCH_2CH_2O_2CC(CH_3)=CH_2$  wherein  $n$  is 4, 6, 8, 10 and 12 in the weight ratio 35/30/18/8/3, average molecular weight 522, prepared by following the procedure of Example II of Fasick and Reynolds, U.S. Patent 3,282,905, using the alcohols



These alcohols were prepared by utilizing the procedure of Parsons, U.S. Patent 3,234,294 to prepare



the procedure of Haszeldine, J. Chem. Soc., 1949, 2856 to prepare  $CF_3CF_2(CF_2)_nCH_2CH_2I$  and the procedure of Day, U.S. Patent 3,283,012 to prepare the alcohols them-

selves. Alternatively, the esters may be prepared from the iodides  $CF_3CF_2(CF_2)_nCH_2CH_2I$  using the procedure of Fasick, U.S. Patent 3,239,557.

Example 1.—Several polymers were prepared using the procedure below and having the compositions shown in Table I. The procedure is as follows:

To 118 parts water at 50° C. to 55° C. was added and mixed a preformed mixture of 11.8 parts dimethyloctadecylamine and 7.1 parts acetic acid. After mixing was complete, 200 parts of a mixture of



and commercial methyl acrylate (ratios indicated in Table I) were added, care being taken to prevent volatilization of methyl acrylate. The resulting mixture was stirred until emulsified.

The resulting emulsion of monomers was purged with nitrogen for one hour, then added to 200 parts air-free deionized water along with 66 parts of water rinse. Then 0.503 part commercial 2-hydroxyethyl methacrylate, 0.840 part of a 60% by weight aqueous solution of N-methylol acrylamide and dodecylmercaptan as indicated in Table I were added. After the resulting mixture was heated at 65° C. for 0.5 hour, a mixture of 0.08 part azobis(isobutyramidine)dihydrochloride in 0.25 part water was added to initiate the polymerization. The temperature was allowed to adjust to 70° C. and the reaction mass was maintained for 4 hours with agitation. The mass was then cooled to ambient temperature, giving an emulsion containing about 25% by weight polymer. The monomer ratio in the polymers was the same as the ratio of monomers used.

In the examples 1-K, methyl methacrylate was substituted for the methyl acrylate in the above procedure.

TABLE I

	Parts—			
	FM <sup>1</sup>	MA <sup>2</sup>	MMA <sup>3</sup>	DDM <sup>4</sup>
Number:				
1-A	190	10	0	1.6
1-B	180	20	0	1.6
1-C	170	30	0	1.6
1-D	160	40	0	1.6
1-E	150	50	0	1.6
1-F	140	60	0	1.6
1-G	170	30	0	0.08
1-H	170	30	0	1.6
1-I	170	30	0	0.08
1-J	150	50	0	1.6
1-K	150	0	50	1.6

<sup>1</sup>  $CF_3CF_2(CF_2)_nCH_2CH_2O_2CC(CH_3)=CH_2$ .

<sup>2</sup> Methyl acrylate.

<sup>3</sup> Methyl methacrylate.

<sup>4</sup> Dodecylmercaptan.

Example 2.—Each of the above-prepared emulsions were diluted with water to contain sufficient polymer to provide 6.21%



in polymerized form in the emulsion, i.e., all emulsions then had equal fluorine content. Each emulsion was padded on nylon tricot automobile upholstery at 1.5% on weight of fabric of the emulsion, i.e., 0.093% polymerized  $CF_3CF_2(CF_2)_nCH_2CH_2O_2CC(CH_3)=CH_2$  on weight of fabric. Each pad bath also contained 0.06% "Mykon" NRW-3, a non-rewetting thermally unstable nitrogen compound, Sun Chemical Corp., and 3.0% isopropyl alcohol on weight of bath. The treated nylon samples were then dried and cured at 380° F. for 100 seconds.

Additionally, there was applied to separate fabric samples of the same type, "Scotchgard" FC-214, a product of Minnesota Mining and Manufacturing Co., at 0.45% on weight of fabric of each of the two components parts A and B of said "Scotchgard" product, the "Mykon" NRW-3 and isopropyl alcohol being the same as above. The treated nylon was cured in the same manner as above.

Water repellencies of the treated fabrics were determined using Test Method 22-1964 of the American Association of Textile Chemists and Colorists. A rating of 100 denotes no water penetration or surface adhesion, a

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rating of 90 denotes slight random sticking or wetting and so on.

Oil repellency was determined by Test Method 118-1966T of the A.A.T.C.C., this test comprises placing a drop of test solution carefully on the textile on a flat horizontal surface. After thirty seconds, any penetration or wicking into the fabric is noted visually. The nature of the test solutions is shown below; Nujol, of course, is a purified petroleum oil. Anything with a rating of five or greater is good or excellent, anything with a rating of one or over can be used for certain purposes. As an example, if a treated fabric repels the Nos. 1-6 solutions but not the number 7 solution, its rating is 6.

Oil repellency rating	Test solution	Surface tension, dynes/cm. at 25° C.
8	n-Heptane	20.0
7	n-Octane	21.8
6	n-Decane	23.5
5	n-Dodecane	25.0
4	n-Tetradecane	26.7
3	n-Hexadecane	27.3
2	65/35 hexadecane-"Nujol"	29.6
1	"Nujol"	31.2

Resistance to dry soiling was tested by a method perfected by the Ford Motor Company. The procedure is as follows:

A sample, 5 x 5 inches, of each treated fabric is prepared. A light reflectance reading is taken using the Color-master Differential Colorimeter, Meeco Instrument Manufacturing and Engineering Equipment Corp., Warrington, Pa., using the filter which gives the highest reflectance reading. A 5 x 5 inch card stock template having a 1 x 1 inch square hole in the center is then placed on the sample and 0.1 g. of synthetic soil is applied through a 40 mesh sieve. The sample, template and covering 96 x 100 thread white cotton cloth are then clamped to a 4 x 6 x ¾ inch urethane foam block and placed in a pilling tester (Custom Scientific Instruments, Inc., Arlington, N.J., catalog No. CS-53041). A 2 x 2 x ¾ inch urethane foam block covered with the same cotton cloth is placed in the floating rack. The floating block is passed back and forth over the covered test sample for two minutes. The pilling tester machine requires modification to take the urethane foam blocks. Loose soil is then removed from the sample by holding a 50 p.s.i. air nozzle on the fabric and moving it back and forth over the fabric once each in the warp and filling directions. A reflectance reading is then taken in the soil area. The percent soiling is then determined by the equation

$$\text{percent soiling} = \frac{R_1 - R_2 \times 100}{R_1}$$

where  $R_1$  is reflectance before soiling and  $R_2$  after soiling.

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The synthetic soil was the so-called "Cyanamide Soil" and had the following composition:

Material:	Weight percent
Peat moss -----	38
Cement -----	17
Kaolin clay -----	17
Silica, 200 mesh -----	17
Furnace black -----	1.75
Red iron oxide -----	0.50
Mineral oil -----	8.75

The results obtained are shown in Table II below. Resistance to soil is represented by low percent soiling:

TABLE II

15	Polymer number:	Repellencies		Percent soil
		Oil	Water	
20	1-A	3	90	12.4
	1-B	4-5	90	10.8
	1-C	4-5	90	9.3
	1-D	5	70	9.7
	1-E	5	70	12.5
	1-F	5	70	12.5
	1-G	3	90	12.4
	1-H	5	90	7.6
	1-I	3-4	80	9.5
25	FC-214	5	100	12.9
	Untreated	0	0	29.9

Several things are apparent from the data of Table II. First, the best soil resistance is normally obtained at about 30-40 parts methyl acrylate based on the example or 15-20 parts based on a total of 100 parts of FMA and MA for each polymer, i.e., 1-C, 1-D, 1-H and 1-I. Second, molecular weight has an effect on dry soil resistance; as can be seen by comparing the results with polymers 1-C and 1-H which used the larger amounts of dodecylmercaptan in their preparation and hence have lower molecular weights than polymers 1-G and 1-I which used small amounts of mercaptan.

Example 3.—Formulations of polymers 1-J and 1-K were prepared having the following compositions:

Formulation	Percent*					
	1	2	3	4	5	6
Polymer 1-J	1.5		2.5		3.5	
Polymer 1-K		1.5		2.5		3.5
"Mykon" NRW-3	0.05	0.05	0.05	0.05	0.05	0.05
Isopropyl alcohol	3.0	3.0	3.0	3.0	3.0	3.0

\*Polymers, on weight of fabric, percent emulsion, see Ex. 2. "Mykon" NRW-3 and isopropyl alcohol on weight of bath.

Formulations 1 and 2 were padded on nylon auto fabric at the indicated concentrations. Formulation 3-6 were padded on Thermosol dyed 65/35 polyester/cotton poplin and undyed, mercerized cotton poplin. The treated fabric samples were placed in a curing oven heated at 275° F. for varying periods of time. The samples of fabric were then air dried at room temperature to constant weight and tested for oil and water repellency by the methods described earlier. The results are shown in Table III below:

TABLE ID

[illegible]

It is readily seen in Table III that polymer 1-J, which is within the scope of this invention, rapidly develops oil repellency on all three fabrics whereas polymer 1-K, based on methyl methacrylate and without the scope of this invention, does not. In considering Table III, it should be noted that the nylon fabric takes about 20 seconds to dry in the oven, the polyester/cotton about 40 seconds to dry and the cotton poplin even longer. Obviously, the fabric temperature will not exceed 212° F., the boiling point of water, until the fabric is dry. There is a great advantage to having oil repellency develop merely by drying since it provides the treated textile with protection prior to cure hence prevent damage due to accidental contact with oils during handling. It is entirely unexpected that changing from a methyl acrylate monomer to methyl methacrylate monomer should have such marked effect.

The foregoing detailed description has been given for clarity of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to exact details shown and described for obvious modifications will occur to one skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An oil- and water-repellent and dry soil resistant aqueous emulsion polymer consisting essentially of

(a) from about 70 to 95 parts of units derived from monomers having the structure



where  $R_f$  is a perfluoroalkyl group of 4 to 14 carbon atoms;

(b) from about 30 to 5 parts of units derived from methyl acrylate or ethyl acrylate monomers, wherein the total weight of the units derived from (a) and (b) present in the polymer is 100 parts; and

(c) from about 0 to 1 part of units derived from monomers selected from  $CH_2=CRCONHCH_2OH$ ,



and mixtures thereof, wherein R is H or  $CH_3$ , said polymer having been prepared in the presence of from

about 0.04% to 1.0% of a chain transfer agent based on the total weight of the monomers.

2. An aqueous emulsion polymer according to claim 1 wherein  $R_f$  in the units defined in part (a) of claim 1 has the formula  $CF_3CF_2(CF_2)_n$ — wherein  $n$  has the numerical values 4, 6, 8, 10 and 12 present in the approximate weight ratio 35/30/18/8/3.

3. An aqueous emulsion polymer according to claim 1 wherein R in the units of  $CH_2=CRCONHCH_2OH$  in part (c) of claim 1 is H—.

4. An aqueous emulsion polymer according to claim 1 wherein R in the units  $CH_2=CRCO_2CH_2CH_2OH$  in part (c) of claim 1 is  $CH_3$ —.

5. An aqueous emulsion polymer according to claim 1 wherein the monomer of part (b) of claim 1 is methyl acrylate.

6. An aqueous emulsion polymer according to claim 1 consisting essentially of

(a) about 85 parts of units derived from



(b) about 15 parts of units derived from methyl acrylate, and

(c) a mixture of about 0.25 part of units derived from N-methylol acrylamide and 0.25 part of units derived from 2-hydroxyethyl methacrylate.

7. A textile fabric treated with an aqueous emulsion polymer of claim 1.

8. A textile fabric treated with an aqueous emulsion polymer of claim 2.

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