ABSTRACT

Water is dispersed in inert, non-polar fluorocarbon with a non-ionic emulsifier which is soluble in the water and fluorocarbon and contains a hydrophobic fluoroaliphatic portion and a hydrophilic solubilizing portion, to provide a water-in-fluorocarbon emulsion useful in the dyeing of textiles.

11 Claims, No Drawings

References Cited

UNITED STATES PATENTS

3,129,053 4/1964 Castle ..................................... 8/93

Primary Examiner—Donald Levy
Attorney, Agent, or Firm—Alexander, Sell, Steldt & Delahunt
WATER-IN-FLUOROCARBON EMULSION

This invention relates to emulsions of water in fluoro-
carbon, to the preparation of said emulsions, and to the
use of said emulsions in the dyeing of textiles.

The use of organic solvents in the dyeing of textiles
is well-known (see "Review of Progress in Coloration," Vol.
II, p. 42, May, 1971, Society of Dyers and Colorists,
London, England). With the growing awareness of
water pollution and environmental problems, increasing
attention has been given to this process (see "Textile
solvents evaluated for this purpose include perchloro-
ethylene, which is strongly absorbed by some textiles
and consequently is not readily removed and recov-
ered. Most of the dyes used have substantial solubility
in these solvents, requiring relatively high concentra-
tion initially, because of the relatively poor partition
coefficient between solvent and fiber, and the relatively
large fraction of the dye which is retained in the solvent
and remains as unrecoverable residue after the distilla-
tion step of the solvent recovery.

Recently, some fluorinated materials have been pro-
posed for use in dyeing in lieu of organic solvents.
Characteristically, such fluorinated materials are sub-
stantially inert to the dyes and the textile fabrics in-
volved and they neither dissolve in the textile fabric nor
show any substantial dissolving power toward the dyes.
Rather than a mere physical mixture of dye and fluori-
nated material, a small amount of water is dispersed
throughout the fluorinated material. Dyes are asso-
ciated primarily with the water phase and are retained
with the water by the fabric. Substantially all of the fluo-
nated material, in fairly pure form, is recovered from
the process, and almost all of the dye supplied to the
system remains on the fabric. Although even slight
losses of the relatively expensive fluorinated material
would be economically significant, such unavoidable
losses are more than compensated for by the increased
efficiency of dye utilization.

Since transfer of the dye to the fabric is dependent on
the adsorption or absorption of the aqueous phase by
the fabric, uniformity of the dye depends upon uniform
pickup of water by the fabric. This, in turn, requires a
dispersion of very fine water droplets throughout the
fluorinated material. The dispersion must be suffi-
ciently stable to prevent agglomeration of water parti-
cles in those parts of the system where agitation is at
a minimum, as within the confines of the fabric itself.
Establishment and maintenance of such a fine, stable dis-
persion requires a suitable dispersing agent or emulsi-
fier.

Conventional emulsifiers, in which the hydrophilic
portion is nonionic, anionic, or cationic and the hydro-
phobic portion is hydrocarbon in nature, tend to pro-
duce either a very unstable emulsion or an emulsion in
which the water is the continuous phase and the fluori-
nated material is the discontinuous phase. As the
amount of water is decreased, particularly to where
there is substantially less water than fluorinated mat-
erial, this results in stiff pastes which are unsuitable for
pumping or adequate penetration of the fabric.

Briefly, in one aspect of this invention, relatively sta-
bile water-in-fluorocarbon emulsions, useful as carriers
for dyes in the dyeing of textiles, are provided by using
as the emulsifier an inert, non-ionically emulsifier which
is soluble in the fluorocarbon phase and contains one or
more fluoroaliphatic non-polar hydrophobic moieties
and also contains one or more solubilizing hydrophilic
nonionic moieties which render the emulsifier soluble
or even miscible in water.

The fluoroaliphatic moieties in the emulsifiers used in
this invention are generally monovalent aliphatic
moieties. They can be straight chain, branched chain,
and, if sufficiently large, cyclic, or combinations
thereof, such as alkylecycloaliphatic radicals. At least
75 percent of the non-catenary carbon valence bonds
in the fluoroaliphatic moiety are attached to fluorine
atoms. The fluoroaliphatic skeletal chain can include
catenary oxygen and/or trivalent nitrogen hetero atoms
bonded only to carbon atoms, such hetero atoms pro-
viding stable linkages between fluorocarbon groups
and not interfering with the inert character of the
fluoroaliphatic moiety or radical. While fluoroaliphatic
moiety can have a large number of carbon atoms, not
more than 20 carbon atoms will be adequate and pre-
ferred since larger radicals usually represent a less effi-
cient utilization of fluorine than is possible with smaller
fluoroaliphatic moieties. Generally, the fluoroaliphatic
moiety will have 3 to 20 carbon atoms, preferably 6 to
about 12, and will contain 40-78 weight percent, pre-
ferably 50-77 weight percent, carbon-bonded fluorine.
While the fluoroaliphatic moiety can be completely flu-
orinated, e.g. as in the case of a C₆F₁₄ radical, up to
25 percent of the substituents on the carbon chain can
be non-ionic, non-polar substituents such as chlorine,
halogen, or hydrogen atoms, such substituents not ad-
versely affecting the stability of the emulsifier molecule
nor its solubility in the fluorocarbon phase, which can
be as low as 0.01 weight percent.

The water solubilizing moieties in the emulsifiers
used in this invention are polar hydrophilic moieties
which are non-ionic, since the ionic hydrophilic moi-
eties which are non-ionic, since the ionic hydrophilic
moieties have a tendency to form fluorocarbon-in-
water emulsions under most conditions. The solubiliz-
ing moiety is generally a monovalent organic radical,
such as a polyester moiety or, preferably, a poly(ox-
yalkylene) moiety, the nature and hydrophilicity of the
solubilizing moiety being such as to render the emulsi-
fier soluble in water at 25°C. to the extent of at least 0.1
weight percent. Solubilization may even be strong
enough to render the emulsifier miscible with water.
For those emulsifiers only slightly soluble in water,
compatibility can be determined by measuring the solu-
bility of water in the emulsifier.

The fluoroaliphatic hydrophobic moieties can be
bonded or linked to the hydrophilic moieties by va-
lence bonds or by any suitable linkage or radical which
is free of polar groups, such as hydroxyl, carboxyl, and
the like, and is stable to hydrolysis under conditions
the emulsion is used. The linkage between the two moieties
can be a polyvalent aliphatic linkages, e.g. —CH₂CH-
—H₂ and —CH₃CH(CH₃)=CH₂, polyvalent aromatic, e.g.

\[
\begin{align*}
&\text{CH₃} \\
&\text{CH₂} \\
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&\text{CH₂} \\
&\text{CH₃}
\end{align*}
\]
preparation of such an emulsifier and the availability of necessary precursors thereof.

The emulsifiers used in this invention will contain 30 to 60 weight percent carbon-bonded fluorine, the fluorine content of the emulsifier residing in said fluorolaliphatic moieties to insure adequate solubility of the hydrophobic moieties in the fluorocarbon phase of the emulsion. The fluorolaliphatic moieties and hydrophilic moieties are balanced to assure solubility of the emulsifier in water and the fluorocarbon phase. Generally this balance will be achieved, in the case of emulsifiers where the principle solubilizing moiety is poly(oxyethylene), when the fluorolaliphatic moieties contain a total of 3 to 20 fluorinated carbon atoms and the number of oxyethylene units is in the range of 2 to 25.

One class of emulsifiers useful in preparing the water-in-fluorocarbon emulsions of this invention can be represented by the general formula:

\[(R_n)_mQ_z(A)n\]

where

- \(R\) is a fluorolaliphatic hydrophobic radical;
- \(Q\) is a solubilizing hydrophilic monovalent non-ionic organic radical;
- \(A\) is a linkage through which \(R\) and \(Q\) are covalently bonded together; and
- \(m\), \(n\), and \(z\) are integers of 1 to 3.

A particularly useful class of emulsifiers is that expressed in terms of the formula:

\[(R_n)_mQ_z[(CH_2CH_2O)_y]A\]

where \((CH_2CH_2O)_y\) is a polyoxyethylene chain, \(x\) being the average number of oxyethylene units in the chain, such number being from 1 to 25, preferably 2 to 10, \(A\) is a monovalent organic radical or a hydrogen atom, and \(R\), \(Q\), \(m\), \(n\), and \(z\) are as defined above.

Some of the emulsifiers falling within the scope of the above formulas are known in the art, e.g., U.S. Pat. Nos. 2,915,554 (Ahlbrecht and Morin), and 3,470,258 (Tesoro). The emulsifiers with poly(oxyalkylene) solubilizing moieties can be obtained by several methods, such as by the oxalkylation or condensation of ethylene oxide and 1,2-propylene oxide with fluorine-containing compounds having at least one Zerewitinoff active hydrogen atom, e.g. \(R_2SO_2N(R')(CH_2)CH(\text{OH})C\text{H}_2OH\), where \(R'\) is lower alkyl or hydrogen. Said oxalkylation can be accomplished by known procedures, e.g., as described in U.S. Pat. No. 2,915,554 (Ahlbrecht and Morin), to produce emulsifiers used in this invention. Various fluorolaliphatic compounds containing functional groups, e.g., hydroxyl, amino, imino, mercapto and carboxyl, with active hydrogen atoms which can be oxalkylated to produce emulsifiers useful in this invention are disclosed in U.S. Pat. Nos. 3,094,547, 3,128,272, 3,217,035, 3,378,399, 3,398,182, 3,450,755, 3,458,571, 3,478,116, 3,484,281, 3,510,455.

Generally, because the starting fluorolaliphatic compounds will be obtainable as mixture of isomeric and homologous compounds, and the methods used to prepare the hydrophilic moiety result in a range of materials of similar composition, the emulsifiers used in this invention will be a mixture of compounds whose average composition is described by the formulas given above.

The fluorocarbon phase of the emulsions of this invention is stable, inert, non-polar, oleophobic and hydrophobic, highly fluorinated liquid and usually will be a mixture of compounds having such nature. The fluorocarbons can be straight chained, branched, or cyclic, or a combination thereof, such as alklycycloaliphatic, therm can be saturated or unsaturated, and hydrophilic unsaturated.

The skeletal chain of the fluorocarbon can include catenary oxygen and or trivalent nitrogen hetero atoms bonded only to carbon atoms, such hetero atoms providing stable linkages between fluorocarbon groups and not interfering with the inert character of the fluorocarbon. The fluorocarbon has about 6 to about 25 carbon atoms, the maximum number of carbon atoms being dictated by the desired volatility for processing ease. Generally, the fluorocarbon will have a boiling range between 55°C and 200°C, preferably 90°C to 150°C.

Generally, the fluorocarbon will contain about 60 to 76 weight percent carbon-bonded fluorine. The fluorocarbon can contain some hydrogen or chlorine, i.e. less than about 5 atom percent on the basis of fluorine content, but is preferably substantially completely fluorinated.

Fluorocarbons useful in this invention are known and readily available, usually as mixtures of fluorocarbons. U.S. Pat. Nos. 3,250,807; 3,250,808, and 3,274,239 disclose fluorinated oils, made by polymerization of perfluoropropyene oxide, which can be stabilized, e.g. as disclosed in U.S. Pat. Nos. 3,214,478, 3,242,218, and 3,342,875, to provide fluorocarbons useful in this invention, said stabilization converting functional or active end groups to inert carbon-bonded hydrogen or fluorine by reaction with fluorinating agents, protic bases, or ultraviolet radiation. U.S. Pat. Nos. 2,500,388, 2,519,983, 2,594,272, and 2,616,927 describe the preparation of inert, highly fluorinated compounds, such as hydrocarbons, ethers, and tertiary amines, said preparation involving electrochemical fluorination in anhydrous HF medium. Commercial fluorocarbons useful in this invention are 3M Company’s “Fluorinert” liquids, e.g. FC-40, FC-43, and FC-48, described in that company’s bulletins Y-ILBG(R) (87-1) RC and Y-IFC-48(60.2) R.

In preparing the emulsions of this invention, the emulsifier can be added to the water component or to the fluorocarbon component, and the two components mixed with agitation in any suitable fashion. The relative amount of the water component emulsified in the fluorocarbon component can vary from as much as a few weight percent to as much as 50 weight percent, based on the total weight of the emulsion.

The water-in-fluorocarbon emulsions of this invention are relatively stable. Standing at room temperature, the emulsions generally do not separate into their two phases in less than about 15 minutes, although emulsions which separate in a short a period of time as ½ to 3 minutes can be used under conditions of continuous agitation.

As mentioned earlier, the emulsions of this invention are particularly suitable in the dyeing of textiles. To prepare the emulsions for this purpose, the dye can be suspended in the fluorocarbon and the water and emulsifier subsequently added, or the water, emulsifier, and dye can be mixed and added to the fluorocarbon with suitable agitation. The emulsion can be made up in a separate reservoir and subsequently added to the dyeing vessel or the fluorocarbon vessel can be circulated through the dyeing vessel and the water-dye-emulsifier mixture added to the circulating fluid through, for example, a centrifugal pump which can provide the agita-
tion necessary for adequate dispersion. It is generally preferable to prepare the complete emulsion prior to contact with the fabric. In this system, the dyes, because of their generally more polar nature, associate themselves with the aqueous phase and the fluorocarbon phase remains relatively free of both water and dye.

The relative amount of the water, fluorocarbon, and emulsifier components in the emulsion will vary, depending upon the particular class of fabrics used, the temperatures and times desired for treatment, and the specific dye involved. While the process is applicable to both batch and continuous processes, batch processing is conventional and will be used for the illustrative discussion. Generally sufficient fluorocarbon must be used to at least fill the system in the presence of the fabric to be treated, including sufficient to fill the reservoirs, connecting piping, pumps and other auxiliary equipment. The amount of dye used depends upon the particular fabric and the dye and the intensity of color desired. A mixture of dyes can be used to provide special effects or to provide suitable coloration of fabrics composed of a mixture of fibers. Generally an amount of dye between about 0.2 and 5 percent by weight of the fabric is sufficient. The amount of water used depends not upon the amount of fluorocarbon present but on the amount of water required to uniformly wet-out the fabric. If too little water is used, only a portion of the fabric will be wet and only this portion will be dyed. Conversely, if too much water is used, an aqueous phase will remain after dyeing is complete, and this aqueous phase will retain dye. Such unused dye represents uneconomical loss and gives rise to pollution problems. It is not necessary to provide as much water as fabric can possibly hold. In general, the amount of water to be used as an aqueous phase will be about 10 to 100 percent, preferably 15 to 50 percent, by weight of the fabric. It is necessary that the water retain substantially all of the dye added to the system. The amount of emulsifier to be used will be sufficient to provide the emulsion with the desired degree of stability, which will depend on conditions of use of the emulsion, e.g., the degree of agitation, mode of transport, equipment used for dyeing, etc. Generally, the amount of emulsifier will be about 1 to 25 weight percent, preferably 2 to 10 weight percent, based on the weight of the water phase.

The process is suitable for any of the dyeable textile fabrics, such as those based on cotton, wool, rayon, acetate, polyamide, polyester, polycrylonitrile or mixtures of such fibers. Because of the difficulties of dyeing by present techniques, the method is particularly suitable for dyeing of fabrics based wholly or in part on polyester fibers, such as poly(ethylene terephthalate) fibers.

The dyes are suitably those presently used to dye industrial and decorative fabrics, including those used for garments, drapery and upholstery. The dyes (including pigments) suitable for use in this invention are those which are water-wettable in the presence of fluorocarbon. While the process is suitable for use with substantive dyes, such as the conventional acidic or basic dyes, it is particularly beneficial in the application of disperse dyes, which have relatively low or moderate solubility in water and which require subsequent elevated temperature processing to insure satisfactory leveling, penetration, and permanence. Because of the much greater efficiency of application to the fabric, deep shades require the same amount of dye on the fabric as in conventional processes, but substantially less dye is used overall due to substantially complete retention of dye by the fabric.

In addition to the fluorocarbon, water, emulsifier, and dye components of the system, modifying and assisting components such as penetrants, carriers, levelers, and the like, as normally used in the dyeing industry, can also be added to the emulsion, although generally their use need not be as closely controlled, nor are such large quantities required, because of the improved efficiency of the process.

Since, unlike the chlorinated solvents, the fluorocarbon has little or no solvent power toward oils, sizes, and other possible contaminants on the fiber, it is desirable that the fabric be thoroughly scoured prior to dyeing. It is not desirable to combine the scouring and dyeing steps into a single operation, as is sometimes done in present solvent dyeing operations.

It is frequently feasible, except in the case of very sensitive dyeing, to merely remove the fabric, add water, dye and emulsifier to the spent fluorocarbon and repeat the dyeing step on a new piece of fabric. Otherwise, the spent fluorocarbon can be recovered by a simple distillation step and reused, any contaminants, dye and emulsifier aid remaining in the residue from the distillation.

Objects and advantages of this invention are illustrated in the following examples, but it should be understood that various materials and amounts thereof recited in these examples, and other conditions and details, should not be construed to unduly limit this invention.

EXAMPLE 1

Into a one-litre glass cylinder with an outlet built at the bottom of the cylinder and an inlet at the top, the inlet and outlet being suitably connected by polyvinyl chloride tubing to a centrifugal pump, was placed 400 ml. of a mixture (commercially available as fluorinert FC-82) of isomeric fluorocarbons having a composition corresponding to C₃F₇O and C₄F₈ and 0.8 gram of emulsifier, C₆H₅SO₃N(C₄H₈)₃C₆H₅O(C₂H₄O)₈H, and 8 grams of water in which was suspended 0.124 gram of SET YELLOW 4R (Color Index No. 26074), a disperse dye. The circulating pump was operated until a stable emulsion was obtained, about 2 min. Twenty grams of an undyed piece of rayon-acetate velvet was loosely rolled and placed in the cylinder. Pumping was resumed. Within 5 min. a uniform deposition of the dye was obtained over the whole piece of fabric and substantially all of the water was absorbed, leaving a clear, almost colorless fluorocarbon phase. The dyed fabric was then dried and the dried fabric retained its uniformity of color.

EXAMPLE 2

Using the equipment of Example 1, a water-fluorocarbon emulsion was formed from 400 ml. of a C₃ fluorocarbon mixture (boiling at about 100°C. and commercially available as “fluorinert” FC-77), 0.2 g. of the emulsifier of Example 1, 4 ml. of water, and 0.15 g. of the dispersed dye Amocel Pink B (Color Index No. 60710). Fifteen g. of white polyester fabric was inserted in the cylinder and circulation continued until the dye was absorbed on the fabric, dye deposition
being uniform throughout the fabric. The remaining fluorocarbon phase was clear and essentially colorless.

**EXAMPLE 3**

Using the equipment of Example 1, a water-in-fluorocarbon emulsion was formed by adding to 400 ml. of fluorinert FC-77 (in which was dissolved 0.35 g. of the emulsifier used in Example 1) a solution of 0.75 g. Na$_2$SO$_4$, 0.75 g. of a 25 percent aqueous acetic acid, and 0.15 g. of Acid Red 27 (Color Index No. 16182). The emulsion was used to dye 20 g. of white woolen gaberdine fabric. After 30 minutes of circulation, the fabric was uniformly dyed and the remaining fluorocarbon was clear and essentially colorless.

**EXAMPLE 4**

Three water-in-fluorocarbon emulsions were prepared by different techniques using a C$_x$ fluorocarbon mixture with a boiling point of about 100°C. (commercially available as "FC-77") and the emulsifier used in Example 1.

In the first run, 50 ml. of the fluorocarbon was placed in a bottle and 0.125 g. of the emulsifier was added. The emulsifier dispersed well in the fluorocarbon. Water in the amount of 2.5 ml. was added to the fluorocarbon-emulsifier and the mixture was shaken to produce a milky dispersion of water in fluorocarbon. The water phase separated on standing but was readily dispersed by gentle agitation.

In the second run, a high speed, high shear mechanical agitator ("Dispersador") was used to prepare the emulsion, with similar results.

In a third run, 150 ml. of fluorocarbon was placed in a stirred glass pressure reactor and 0.75 g. of the emulsifier was added with agitation. Water in the amount of 7.5 ml. was added. The mixture was vigorously agitated by a bladed stirrer while the reactor was heated in a 126°C oil bath, the reactor pressure being about 3 atmospheres. A milky dispersion of low viscosity was obtained.

**EXAMPLE 5**

The first run of Example 4 was repeated twice using an emulsifier of the formula C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)C$_2$H$_2$O(C$_2$H$_4$)$_2$H, in one run x being 1 and in the other run x being 10. Results obtained were similar to those of Example 1.

**EXAMPLE 6**

The first run of Example 4 was repeated four times using an emulsifier of the formula C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)C$_2$H$_2$O(C$_2$H$_4$)$_2$H, where x varied for each run, viz. 1.29, 4.19, 6.7, and 9.2. The stability of the dispersions was better for the emulsifiers with lower ethylene oxide content.

**EXAMPLE 7**

The first run of example 4 was repeated three times, using in each run different emulsifier, viz. C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)C$_2$H$_2$O(C$_2$H$_4$)$_2$H, C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)C$_2$H$_2$O(C$_2$H$_4$)$_2$H, and C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)C$_2$H$_2$O(C$_2$H$_4$)$_2$H. The dispersions obtained remained stable while gently rolled in the bottle.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiment set forth herein.

What is claimed is:

1. A water-in-fluorocarbon emulsion stabilized with a non-ionic emulsifier containing fluorooaliphatic, non-polar, hydrophobic moiety and non-ionic, hydrophilic, solubilizing moiety, said fluorocarbon being a stable, inert, non-polar, oleophobic, hydrophobic, highly fluorinated liquid having a boiling range between 55° and 200°C. and containing 60 to 76 weight percent carbon-bonded fluorine and less than about 5 atom percent hydrogen or chlorine on the basis of said carbon-bonded fluorine, said fluorocarbon having 6 to 25 carbon atoms and a skeletal chain which is straight chain, branched, cyclic, or combinations thereof and can contain catenary oxygen or trivalent nitrogen hetero atoms, or both kinds of said hetero atoms, said hetero atoms being bonded only to carbon atoms, said fluorooaliphatic moiety of said emulsifier containing 40 to 78 weight percent carbon-bonded fluorine and having 3 to 20 carbon atoms, said fluorooaliphatic moiety being straight chain, branched chain, cyclic, or combinations thereof, and having at least 75 percent of the non-catenary carbon valence bonds attached to fluorine atoms and up to 25 percent of said valence bonds being bonded to non-ionic, non-polar substituents, and wherein the skeletal chain of said fluorooaliphatic moiety can contain catenary oxygen or trivalent nitrogen hetero atoms, or both kinds of said hetero atoms, said hetero atoms being bonded only to carbon atoms, said hydrophilic moiety of said emulsifier having a sufficient degree of hydrophilicity to render said emulsifier soluble in water to the extent of at least 0.1 weight percent.

2. The emulsion of claim 1, wherein the fluorine content of said emulsifier is 30 to 60 weight percent, said emulsifier being soluble in said fluorocarbon to the extent of at least 0.01 weight percent.

3. The emulsion of claim 2, wherein said hydrophilic moiety is poly(oxymethylene) wherein the number of oxymethylene units is in the range of 1 to 25.

4. The emulsion of claim 3, wherein said oxymethylene units are oxethylenic, oxopropylenic, or mixtures thereof.

5. The emulsion of claim 1 further comprising a dye dispersed or dissolved in the aqueous phase of said emulsion.

6. The emulsion of claim 1 wherein said emulsifier is C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)(C$_2$H$_4$O)$_x$H.

7. In a method of dyeing textiles with a water-fluorocarbon medium containing dye, the improvement comprising using as the medium the water-in-fluorocarbon emulsion of claim 5.

8. The method of claim 7, wherein said emulsifier is C$_x$F$_{2x}$SO$_2$N(C$_2$H$_4$)(C$_2$H$_4$O)$_x$H.

9. A water-in-fluorocarbon emulsion stabilized with a non-ionic emulsifier containing fluorooaliphatic, non-polar, hydrophobic moiety and non-ionic, hydrophilic, solubilizing moiety, said fluorocarbon being a stable, inert, non-polar, oleophobic, hydrophobic, highly fluorinated liquid having a boiling range between 55° and 200°C. and containing 60 to 76 weight percent carbon-bonded fluorine and less than about 5 atom percent hydrogen or chlorine on the basis of said carbon-bonded fluorine, said fluorocarbon having 6 to 25 carbon atoms and a skeletal chain which is straight chain, branched, cyclic or combinations thereof and can con-
tain catenary oxygen or trivalent nitrogen hetero atoms, or both kinds of said hetero atoms, said hetero atoms being bonded only to carbon atoms, said fluoroaliphatic moiety of said emulsifier containing 40 to 78 weight percent carbon-bonded fluorine and having 3 to 20 carbon atoms, said fluoroaliphatic moiety being straight chain, branched chain, cyclic, or combinations thereof and having at least 75 percent of the non-catenary carbon valence bonds attached to fluorine atoms and up to 25 percent of said valence bonds being bonded to non-ionic, non-polar substituents, and wherein the skeletal chain of said fluoroaliphatic moiety can contain catenary oxygen or trivalent nitrogen hetero atoms, or both kinds of said hetero atoms, said hetero atoms being bonded only to carbon atoms, said hydrophilic moiety of said emulsifier being poly(oxyalkylene) wherein the number of oxyalkylene units is in the range of 1 to 25 and said oxyalkylene units are oxyethylene or a mixture of oxyethylene and oxypropylene, said hydrophilic moiety having a sufficient degree of hydrophilicity to render said emulsifier soluble in water to the extent of at least 0.1 weight percent, said emulsifier being soluble in said fluorocarbon to the extent of at least 0.01 weight percent, and the fluorine content of said emulsifier being 30 to 60 weight percent.

10. The emulsion of claim 9 further comprising a dye dispersed or dissolved in the aqueous phase of said emulsion.

11. In a method of dyeing textiles with a water-fluorocarbon medium containing dye, the improvement comprising using as the medium the water-in-fluorocarbon emulsion of claim 10.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,792,977 Dated February 19, 1974

Inventor(s) Richard A. Guenthner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, lines 35-37 should read -- which are non-ionic, since the ionic hydrophilic moieties have a tendency to form fluorocarbon-in- --.

Signed and sealed this 5th day of November 1974.

(SEAL)
Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,792,977 Dated February 19, 1974

Inventor(s) Richard A. Guenthner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 41, "fluorinert FC-82" should read -- "Fluorinert FC-82" --;

Column 6, line 43, "C_8F_{16} and C_8F_{18} and" should read -- C_8F_{16} and C_8F_{18} --;

Column 6, line 63, "fluorinert FC-77" should read -- "Fluorinert FC-77" --;

Column 7, line 8, "fluorinert FC-77" should read -- "Fluorinert FC-77" --;

Column 7, line 21, "FC-77" should read -- "Fluorinert FC-77" --.

Signed and sealed this 9th day of July 1974.

(SEAL)

Attest:

McCOY M. GIBSON, JR. C. MARSHALL DANN
Attesting Officer Commissioner of Patents