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METHOD OF DYEING SYNTHETIC FIBROUS MATERIALS

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This invention relates to a method of dyeing hydrophobic synthetic fibers and fabrics and to novel compositions for use therein.

In recent years a number of synthetic fibers have been developed which have very desirable properties. Examples of such fibers are polyglycol terephthalates which is sold by the Du Pont Company under the name "Dacron," various fibers containing polymers and copolymers of acrylonitrile such as for example dry-spun polyacrylonitrile spun from an anhydrous organic solvent such as dimethylformamide and sold by the Du Pont Company under the name of "Orlon," wet-spun acrylonitrile fibers spun from a cold concentrated aqueous thiocyanate solution, various super polyamides such as polyhexamethylene-diamine adipamide and poly ϵ -amino caprolactam which are generally known in the trade as nylons, copolymers of vinyl-acetate and acrylonitrile known as "Dynel," and the like. Despite the important advantageous properties of these new fibers they have disadvantages as many of them are difficult to dye particularly to uniform deep shades. The problem is particularly serious with the dry-spun acrylonitrile polymers and copolymers and with polyglycol terephthalate fibers. As a result many of these fabrics are obtainable only in pastel shades which seriously reduces their field of utility.

A very large number of compounds have been tested as assistants in the dyeing of hydrophobic fibers. Only a few have been actually used and they are far from ideal. They are as follows: phenol, o-phenylphenol, p-phenylphenol, o-dichlorobenzene, monochlorobenzene, benzoic acid and phenyl methyl carbinol. None of the above assistants are really satisfactory from the standpoint of cost, toxicity, disposal, residual effect on the fibers, methods of utilization and effectiveness at normal dyeing temperatures in regular equipment.

Some of the major defects of the types of compounds used as dyeing assistants are the following:

- (1) Phenolics leave residues that impart odor and reduce light fastness.
- (2) Monochlorobenzene is toxic and calls for stringent precautions.
- (3) Benzoic acid is costly and is a mild irritant.
- (4) Phenyl methyl carbinol is expensive and requires an alkaline scour for maximum fastness.
- (5) Almost all of these compounds present a severe disposal problem as their use can result in serious stream pollution.

According to the present invention we have found that an entirely different type of dyeing assistant permits rapid level dyeing of hydrophobic synthetic fibers in deep shades and without the use of special equipment which is not readily available to the dyer. The present invention uses as a dyeing assistant an emulsion of an organic ester of an aromatic monocarboxylic acid. The emulsion is effected by means of a surface active emulsifier. In some ways the emulsion is very critical. In others wide latitude is permissible. The critical factor is the amount of the emulsifier or rather its ratio to the ester. The lower limit is set automatically by the amount of emulsifier which is required to produce an emulsion of the oil-in-water type. No numerical ratio can be given

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for this lower limit as the minimum amount of emulsifying agent will vary with different surface active agents as is well known in the art of preparing emulsions.

An increase in the ratio of emulsifying agent to ester gives somewhat better results but too much emulsifying agent must also be avoided as an excessive amount begins to interfere with the fixation of the dyestuff and results in weaker shades. The upper limit therefore is one part emulsifying agent to two parts of ester. In general the best results are obtained with an amount of an emulsifying agent approximating 10% of the ester. Good results are still obtainable from as little as 1 part of emulsifier to 50 of ester up to 1 part of emulsifier to 5 of ester. While the limits of emulsifier to ester are quite critical at their extremes it will be seen that a reasonably broad range is usable.

The nature of the aromatic carboxylic ester is not at all critical and any emulsifiable ester whether liquid or solid may be used. In the case of liquid esters the emulsion is easily prepared but in the case of solid esters it is normally necessary to dissolve the ester in a suitable solvent, for example, a hydrocarbon such as benzene and toluene, or alcohol, such as butanol, before emulsification takes place. The fact that no additional solvent is necessary makes the liquid esters somewhat preferable although the final results are not materially different so long as good emulsions are prepared. It is apparently the carboxylic acid ester group which effects the improved results because substituents on the aromatic rings appear to have little or no influence, for example there may be substituents such as halogen, nitro, hydroxy, amino, aroyl, and the like.

The extraordinary improvements obtainable by use of oil-in-water emulsions of the aromatic carboxylic acid esters requires absolutely that they be present in the form of an emulsion. If the ester is used without the emulsifying agent the improved results are not obtained and of course as is well known, surface active agents do not act as dyeing assistants for hydrophobic fibers when used alone. It is not known just how the emulsions of the aromatic carboxylic acid esters operate in the dyeing procedure and it is therefore not intended to limit the invention to any theory of action. One possible effect might be that there is a surface solvent action or swelling action of the esters on the fibers. However, if this were the only reason for the improved results it would be expected that the unemulsified esters would also show marked improvement and they do not. Conceivably there may be some other mechanism present but it does seem at least probable that some compatibility of the ester group with the fiber plays a part. However, as pointed out above no theory is advanced for the operation of the present invention.

Typical examples of liquid aromatic carboxylic acid esters which are usable in the present invention are the following: methyl salicylate, methyl benzoate, isopropyl benzoate, β -methoxyethyl benzoate, methyl 2-chlorobenzoate, methyl-p-tertiary-butyl benzoate, and amyl benzoate. The following esters are illustrations of usable solid esters which have to be dissolved in a solvent before emulsification: methyl ester of 3-hydroxy-2-naphthoic acid, ethyl ester of 3-hydroxy-2-naphthoic acid, methyl p-nitro-benzoate, methyl p-hydroxybenzoate, methyl 2,4-dihydroxybenzoate, methyl 3,4-dichlorobenzoate, methyl p-aminobenzoate, methyl 3,4,5-trimethoxybenzoate, methyl tri-methylgallate, methyl p-phenylbenzoate, methyl o-benzoylbenzoate.

Just as the nature of a particular ester is not critical neither is the emulsifying agent. Thus emulsifiers of the three various types, anionic, non-ionic, and cationic, may be used. Typical examples of the anionic type of emulsifiers are sodium dodecyl sulfate, dioctyl sodium sulfosuc-

inate, di-isobutyl sodium sulfosuccinate and disodium mono (7-ethyl-2-methyl undecyl-4) sulfosuccinate. Typical non-ionic emulsifiers are alkylated aryl polyether alcohols such as the condensation product of ethylene oxide and octyl and nonylphenols. Typical cationic surface active agents are quaternary compounds such as stearamido propyl dimethyl hydroxy ethyl ammonium chloride and condensation products of higher alkyl amines such as the amines obtained from acids of tallow condensed with ethylene oxide. In general any of the emulsifying agents are useful even though they may not be completely soluble in the organic esters or in the aqueous phase. Of course, they must be taken up at the interface of the aqueous phase and the droplets of the ester or by definition they are not emulsifiers. There is some advantage in using mixtures of anionic and non-ionic surface active agents as these appear to produce the most stable and satisfactory emulsions.

It is an advantage of the present invention that the emulsions can be prepared in a wide variety of ways:

(1) The emulsifying agent may be intimately mixed or dissolved with the ester after which the mixture is added to an equal volume of water with vigorous stirring whereupon the dyeing assistant is emulsified. The emulsion is then ready for addition to the dye bath.

(2) One component of the emulsifying agent may be dissolved in the ester and the other component dissolved in the aqueous phase, so that when the two are intimately mixed, the emulsifier is first formed in situ after which the ester is emulsified into the aqueous system. An example of this type is the addition of oleic acid to the ester of the aromatic carboxylic acid and the addition of triethanolamine to the aqueous phase described above.

(3) The dye and emulsifying agent may be dissolved in the ester and then emulsified in the aqueous phase.

(4) The dye and part of the emulsifying agent may be dissolved in the ester and then dispersed in the aqueous phase which also contains the remainder of the emulsifying agent.

Regardless of the method used the dyeing assistant must be emulsified with a small quantity of the aqueous phase to form a uniform emulsion before it is added to the dye bath, otherwise level dyeing is not obtained. In other words the emulsification cannot all be carried out in the dye bath itself. This is about the only limitation on the method of preparation and use of the emulsions.

The present invention is not limited to the dyeing of the hydrophobic synthetic fibers with any particular class of dyes and improves the shade with a wide variety of dyes such as acetate dyes, vat acids, sulfur dyes, azoic colors and even organic pigments. Another phase of the invention is the use of the emulsion of the ester in processes of dyeing acid dyes on acrylic fibers by the cuprous ion method.

Another important application of the present invention is to the so called optical bleaching agents or brighteners which are colorless dyes which fluoresce blue under ultra-violet light and which are used in whitening fabrics. Typical examples are 4-methyl-7-diethylaminocoumarin and 4-methyl-7-dimethylaminocoumarin.

Temperature of dyeing although not critical is also a factor in the present invention and constitutes one of the important advantages thereof. Attempts have been made in the past to increase the rate of dyeing and depth of shade by employing a higher temperature and many dyeings have been effected at temperatures above the boiling point of water going up as high as 280-300° F. This has in fact produced improved results but at considerable off-setting disadvantages. In the first place these high temperatures sometimes injure the fiber and in the second place they add greatly to the cost of dyeing because of the additional expense of operating under pressure. The present invention can be used in such high temperature dyeings above the boiling point of water but it is an important advantage that by means of the present invention

satisfactory dyeing in deep shades can be obtained at much lower temperatures, going down even as far as 160° F. The economic advantages of these lower temperatures make this aspect of the present invention preferred although, of course, it is not limited thereto.

The invention will be illustrated further in the following specific examples in which the parts are by weight unless otherwise specified. In order to avoid the repetition of the formulas of dyes which have not received an official color index number, they will be referred to in the specific examples by their prototype number, and a formula index of the prototypes is presented at the end of the specification.

Example 1

550 parts of polyglycolterephthalate fabric were entered into a Hunter (Reel) machine containing 40,000 parts of water.

20 parts of dioctyl sodium sulfosuccinate and 20 parts of the reaction product of p-octyl phenol and 10 mols of ethylene oxide were dissolved in 400 parts of methyl salicylate. This solution was then emulsified in 440 parts of water with stirring, forming an oil-in-water emulsion. 720 parts of the emulsion were then added to the bath in the dyeing equipment and the cloth was worked at 100° F. until a thorough and uniform penetration resulted. 11 parts of a scarlet dye (Prototype No. 244) was then pasted with a small amount of water and added to the dye bath. Thereupon the bath was heated to the boil and the dyeing carried out at this temperature until complete. The dyed fabric was then rinsed, soaped at the boil in a 1/10% soap solution, rinsed and dried. A deep scarlet shade, free of spots, was obtained.

A duplicate dyeing was made following the above procedure except that the methyl salicylate was not emulsified prior to its addition to the dye bath. The dyed fabric was spotty, dull and commercially unsatisfactory.

Example 2

The procedure of the preceding example was followed except that the scarlet dye was replaced by an equal amount of a Bordeaux dye (Prototype No. 238). The material after dyeing, rinsing, soaping, rinsing and drying, was a deep bluish-red shade. When the methyl salicylate was used without being emulsified before adding to the dye bath, a blotchy, uneven, completely unsatisfactory product was obtained.

Example 3

The procedure of Example 1 was repeated using the same amount of a series of dyes in place of the scarlet. The dyes were as follows:

- a. Green 2B (Prototype 229)
- b. Orange 3RC Ex. Conc. (Prototype 174)
- c. Pink B (Prototype 234)
- d. Yellow GC (Prototype 242)
- e. Violet B (Prototype 241)
- f. Blue dye (Prototype 227)
- g. Pink dye (Prototype 235)
- h. Brown dye (Prototype 230)

In each of the above dyeings when the emulsion of the ester was used, deep level, uniform shades of commercial acceptability were obtained. When the methyl salicylate was used without the presence of the emulsifying agent, blotchy, dull, commercially unsatisfactory dyeings were obtained.

Example 4

The procedure of Example 1 was repeated replacing the methyl salicylate with a corresponding amount of methyl benzoate. The results obtained were substantially the same, the fabric dyed a deep uniform scarlet shade.

When a dyeing was made using the methyl benzoate without the presence of the emulsifying agents, a spotty, dull, unlevel and commercially unacceptable dyeing was obtained.

Example 5

The procedure of Example 1 was repeated except isopropyl benzoate was used instead of the methyl salicylate. The results were generally similar to those obtained in Example 1. A good, commercially acceptable dyeing was obtained.

Example 6

The procedure of Example 1 was repeated except methyl 2-chlorobenzoate was used instead of methyl salicylate. The results were generally similar to those obtained in Example 1. A good, commercially acceptable dyeing was obtained.

Example 7

The procedure of Example 1 was repeated except methyl p-tertiary butyl benzoate was used instead of methyl salicylate. The results were generally similar to those obtained in Example 1. A good, commercially acceptable dyeing was obtained.

Example 8

A number of different synthetic fibers were dyed with the scarlet dye (Prototype 244) of Example 1 using different emulsifying agents. In this example with its table of results and in the remainder of the examples the trade names of the synthetic fibers are used in place of the awkward and much longer chemical designations. Thus polyglycolterephthalate will be referred to as Dacron, dry-spun polyacrylonitrile as Orlon, copolymer of acrylonitrile containing a small amount of vinyl pyridine as Acrilan, wet-thiocyanate spun polyacrylonitrile fibers referred to as X-51 and a copolymer of acrylonitrile and vinyl acetate by the trade name Dynel.

With the exception of the dyeing of Dynel all of the dyeings were made at the boil and they were effected in a dye bath containing 250 parts of water with 0.1 part of dye and 2 parts of methyl salicylate as an oil-in-water emulsion. The emulsion was prepared by dissolving the emulsifying agent listed in methyl salicylate, adding an equal weight of water and agitating to form the oil-in-water emulsion. The emulsion was then added to the dye bath. Five parts of fiber in the form of a skein were entered into the dye bath at room temperature, the temperature raised to the boil, and the dyeing carried out at this temperature until completion. The dyed skeins were then rinsed, soaped, rinsed and dried as described in Example 1. In the case of the Dynel fiber the dyeing temperature was kept below 170° F. as this fiber shrinks at the temperature of boiling water in the presence of the dyeing assistant.

The following table shows the various dyeings of the different fibers with the different emulsifying agents and methyl salicylate. In each case a scarlet shade was obtained of good quality, deep and uniform. Each fabric was check-dyed under exactly the same conditions leaving out the emulsion and much weaker dyeings were obtained with shades from 1/2 to 1/10 as heavy.

Fiber	Part	Emulsifying agent
Dacron.....	0.1	Stearamidopropyl dimethyl hydroxyethyl ammonium hydroxide.
Orlon.....	0.1	Do.
Acrilan.....	0.1	Do.
Dynel.....	0.1	Do.
X-51 filament.....	0.1	Do.
X-51 staple.....	0.1	Diocetyl sodium sulfosuccinate.
	0.1	The reaction product of p-octylphenol and 10 mols of ethylene oxide.
Dacron.....	0.2	Sodium lauryl sulfate.
Do.....	0.2	The reaction product of p-octylphenol and 10 mols of ethylene oxide.
Do.....	0.2	Tallow amine condensed with 5 mols ethylene oxide.
Do.....	0.2	Sodium oleyl methyl taurate.
Do.....	0.2	N-octadecyl disodium sulfosuccinate.
Do.....	0.2	2, 4-di-t-amyl cyclohexyl disodium sulfosuccinate.

Example 9

50 parts of oleic acid were dissolved in 500 parts of methyl salicylate. This was then added with good stirring to a mixture of 500 parts of water containing 20 parts of triethanolamine and an oil-in-water emulsion of the methyl salicylate was obtained. Example 1 was repeated except 770 parts of the above emulsion were used in place of the emulsion described in Example 1. Dacron fabric dyed by this procedure gave level strong shades which were commercially acceptable.

Example 10

2 parts of disodium mono (7-ethyl-2-methyl-undecyl-4) sulfosuccinate were dissolved in 50 parts of water. 50 parts of methyl salicylate were added to this solution with good stirring and an oil-in-water emulsion was formed. 16 parts of this emulsion were added to a dye bath containing 1000 parts of water. 20 parts of Dacron fiber were added and worked at 120° F. until uniform distribution of the emulsion through the fiber resulted. Thereupon 0.4 part of Scarlet BN (Prototype 244) was added to the bath, the temperature raised to the boil and dyeing continued at this temperature until complete. The dyed yarn was removed from the dye bath, rinsed, soaped at the boil in a 0.1% soap solution, again rinsed and dried. A strong level scarlet shade was obtained.

Example 11

50 parts of methyl p-hydroxybenzoate were dissolved in 150 parts of butanol. 2.5 parts of disodium dioctyl sulfosuccinate were then dissolved in the butanol solution after which 2.5 parts of the reaction product of p-octylphenol and 10 mols of ethylene oxide were dissolved in the butanol. The total weight equaled 205 parts. 131 parts of the butanol solution were then added to an equal weight of water with stirring until an oil-in-water emulsion was formed. This emulsion was then added to a laboratory dyeing machine containing 400 parts of water and 40 parts of Dacron fabric were entered and wet-out thoroughly. 0.8 part of Red GG (Prototype No. 236) were pasted in 5-10 parts of water, then further diluted and added to the dye bath. The dye was heated to the boil and dyeing carried out at this temperature until complete. The dyed fabric was then rinsed, soaped at the boil in a 0.1% soaped solution, rinsed and dried. A good, strong red shade was obtained which was level and free from spots.

Example 12

The procedure of Example 11 was followed replacing the methyl p-hydroxybenzoate with same amounts of the series of other esters. Good strong red shades were obtained that were level and free from spots. The other esters were as follows:

- (1) Methyl ester of 3-hydroxy-2-naphthoic acid
- (2) Ethyl ester of 3-hydroxy-2-naphthoic acid
- (3) Methyl tri-methylgallate
- (4) Methyl-3,4-dichlorobenzoate
- (5) Methyl p-phenylbenzoate
- (6) Methyl p-nitrobenzoate
- (7) Methyl o-benzoylbenzoate
- (8) Methyl p-aminobenzoate

Example 13

5 parts of an equal mixture of 4-methyl-7-diethylaminocoumarin and 4-methyl-7-dimethylaminocoumarin were added to 2000 parts of the oil-in-water emulsion described in Example 1. This was then diluted 125 times with water. 5000 parts of Orlon yarn were then entered into the bath and dyed at 120° F. until dyeing was complete. The yarn was then rinsed, soaped at 140° F., rinsed and dried.

A control skein was dyed as described above omitting the oil-in-water emulsion.

The yarn dyed from the bath containing the oil-in-water emulsion was much whiter than the control and fluoresced in ultraviolet light. The dyed control skein did not fluoresce.

Example 14

0.4 part of dioctyl sodium sulfosuccinate and 0.4 part of the reaction product of p-octylphenol and 10 mols of ethylene oxide were dissolved in 8 parts of methyl salicylate. 0.4 part of oil soluble Quinizarine Green (C.I. 1078) was then dissolved in this solution. The solution was stirred with 8 parts of water until a stable oil-in-water emulsion was formed. This emulsion was then added to 1000 parts of water, 20 parts of Dacron fiber entered into the bath which was brought to the boil and dyeing continued at this temperature until complete. The dyed material was then rinsed, soaped, rinsed, and dried. A dark uniform green dyeing was obtained. When a similar dyeing was carried out except that the methyl salicylate emulsion was omitted a light, very uneven dyeing resulted.

Example 15

The procedure of Example 14 was followed replacing the Quinizarine Green with an equal amount of Victoria Blue Base (C.I. 729). A medium shade blue dyeing was obtained.

Example 16

The procedure of Example 14 was followed replacing the Quinizarine Green with an equal amount of 1,4 bis amylamino-anthraquinone. A heavy blue dyed skein was obtained.

Example 17

The procedure of Example 14 was repeated substituting an equal amount of the vat dye salicyl alpha-aminoanthraquinone for the Quinizarine Green. A yellow shade was obtained which showed more than 40 hours light fastness on the fadeometer.

Example 18

The procedure of Example 14 was repeated replacing the Quinizarine Green with an equal amount of Para Toner Y (C.I. 44). A heavy orange shade was obtained.

Example 19

The procedure of Example 14 was repeated replacing the Quinizarine Green with an equal amount of the pigment formed by coupling acetoacetanilide to diazotized m-nitro-p-toluidine. A bright lemon shade was obtained.

Example 20

0.4 part of dioctyl sodium sulfosuccinate and an equal weight of the reaction product of p-octylphenol and 10 mols of ethylene oxide were dissolved in 8 parts of methyl salicylate. This was stirred into 8 parts of water until a stable oil-in-water emulsion was formed. A dye bath was then prepared containing 16 parts of the above emulsion, 1.6 parts of 3-hydroxy-2-naphthoic acid, 1.6 parts of 2-amino 4-chlorotoluene and 1000 parts of water. 20 parts of Dacron were entered into the bath, the temperature raised to the boil and the dyeing continued at the boil, until complete. The yarn was rinsed in cold water and entered into a bath containing 2 parts of hydrochloric acid and 1 part of sodium nitrite together with an additional 1000 parts of water. The temperature was raised to 160° F. and diazotization and coupling continued at this temperature until complete. The yarn was rinsed, soaped at the boil with a solution of 1 g. soap and ½ g. sodium carbonate per liter. The yarn was then rinsed and dried. A deep uniform red shade was obtained. When a similar dyeing was made without the methyl salicylate emulsion, only a light pink shade resulted.

Example 21

The procedure of Example 20 was followed except 0.8 part dianisidine was used instead of the 2-amino 4-chlorotoluene. A deep, uniform, navy shade was obtained. When a similar dyeing was made with the methyl salicylate emulsion omitted, a pale blue shade resulted.

Example 22

The procedure of Example 20 was followed except 0.8 part of m-nitro p-anisidine was used instead of the 2-amino 4-chlorotoluene. A deep uniform Bordeaux shade was obtained. When a similar dyeing was made, except with the methyl salicylate emulsion omitted, a light red shade resulted.

Example 23

The procedure of Example 20 was repeated replacing the 2-amino 4-chlorotoluene with 1 part Black NSHS (Prototype No. 523). A dark gray shade was obtained. When a similar dyeing was made without the methyl salicylate emulsion, only a pastel shade resulted.

Example 24

0.4 part of dioctyl sodium sulfosuccinate and an equal weight of the reaction product of p-octylphenol and 10 mols of ethylene oxide were dissolved in 8 parts of methyl salicylate. This was then stirred into 8 parts of water to form a stable oil-in-water emulsion. The emulsion was added to a dye bath containing 1000 parts of water and 0.8 part of Soluble Vat Scarlet HB (Prototype 107). Twenty parts of Dacron yarn were entered into the bath, the temperature raised to the boil and dyeing continued for about 30 minutes. 0.6 part acetic acid was then added and boiling continued for an equal time. The yarn was then removed from the dye bath, rinsed and developed in a bath containing 2 parts sulfuric acid, 1 part sodium nitrite and 0.2 part sodium dodecyl sulfate dissolved in 1000 parts of water. The temperature was raised to the boil and the skein boiled until the dyeing was complete, whereupon it was rinsed and dried. A heavy, uniformly dyed red dyeing was obtained. In a similar experiment in which the methyl salicylate emulsion was omitted, a very weak dyeing resulted.

Example 25

0.4 part of dioctyl sodium sulfosuccinate and an equal part of the reaction product of p-octylphenol and 10 mols of ethylene oxide were dissolved in 8 parts of methyl salicylate. This was stirred into 8 parts of water until a stable oil-in-water emulsion resulted. The emulsion was then added to 800 parts of water and 20 parts of Dacron polyester yarn entered into the bath and worked at 120° F. until uniform wetting resulted. One part Yellow SCF (C.I. 951) was boiled for 5 minutes with one part sodium sulfide, 0.5 part sodium carbonate and 200 parts water. This was then added to the dyebath. The temperature was then raised to 200–205° F. and the dyeing continued for a short time. Thereupon 6 parts sodium chloride were added and the dyeing continued for about three times as long until complete. The yarn was then removed from the bath, rinsed, and dried. A deep uniformly dyed yellow dyeing was obtained. When a similar dyeing was made, without the emulsion, a very light dyeing resulted.

Example 26

The procedure of Example 25 was repeated except that one part of Brilliant Blue RCF Conc. (C.I. 961) was used in place of the Yellow SCF. A heavy blue dyeing was produced. When the dyeing was repeated eliminating the methyl salicylate emulsion only a pastel shade resulted.

Example 27

0.1 part stearamidopropyl dimethyl hydroxyethyl ammonium hydroxide was dissolved in 5 parts of methyl salicylate. 5 parts of water were added and stirred until a good oil-in-water emulsion formed. This was added to 200 parts of water containing 0.25 part Vat Pink BP (C.I. 1207), 3 parts sodium tripolyphosphate and 2 parts sodium hydrosulfite. 5 parts of Dacron fiber were entered into this dye bath, the bath raised to the boil and the dyeing continued until complete. Thereupon the yarn was removed from the bath, rinsed in cold water, and oxidized at 180° F. in a bath containing 2.5 parts sodium perborate and 250 parts of water. The yarn was again rinsed, then boiled in a bath containing 0.5 part sodium carbonate and 1.0 part soap in 1000 parts water. Again the yarn was rinsed, dried, and a strong pink dyeing obtained. The dyeing had the excellent fastness of the vat dye. When a similar dyeing was made omitting the methyl salicylate emulsion, a very pale pink shade resulted.

Example 28

The procedure of Example 27 was followed except the green vat dye having C.I. 1101 was used instead of Vat Pink 2BP. A strong uniform green shade was obtained. When a similar dyeing was made, except the methyl salicylate emulsion omitted, a very pale green shade resulted.

Example 29

The procedure of Example 27 was followed except Vat Blue 2B (C.I. 1184) was used instead of Vat Pink 2BP. A heavy uniform blue dyeing was obtained. When a similar dyeing was made, except with the methyl salicylate emulsion omitted, a very weak blue dyeing resulted.

Example 30

The procedure of Example 27 was followed except Vat Brown RR (Prototype 121) was used instead of Vat Pink 2BP. A heavy brown shade was obtained. When this experiment was repeated except with the methyl salicylate emulsion omitted, a pale brown shade was obtained.

Example 31

A methyl salicylate emulsion was prepared as described in Example 25 and added to a dye bath containing 1000 parts water, 0.4 part of the chrome complex of the dye-stuff obtained by coupling diazotized 1,2,4 acid on 2-ethoxy benzoylacetoneitrile, 0.8 part sulfuric acid and 0.6 part of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Twenty parts of X-51 acrylic fiber were then entered and the bath raised to the boil. 0.8 part hydroxyl ammonium sulfate was then added and the dyeing continued at the boil until complete. The yarn was removed, rinsed and dried, and showed a heavy uniform bright Bordeaux shade. A similar dyeing was made omitting the methyl salicylate emulsion and a much lighter dyeing resulted which was also much duller in shade.

Example 32

An emulsion was prepared as in the preceding example and added to a dye bath containing 1000 parts water, 0.2 part Milling Green 6B (C.I. 667), 0.2 part formic acid, 0.2 part $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Twenty parts of Dynel yarn were entered into the bath, the temperature raised to 160° F. 0.2 part hydroxyl ammonium sulfate was then added and the dyeing continued until complete. The yarn was then rinsed and dried. A heavy uniform green dyeing being obtained. When a similar dyeing was made omitting the methyl salicylate emulsion, a very pale shade resulted.

FORMULAE OF PROTOTYPE NUMBERS

Prototype number	Formula
5	
121	
10	
174	
15	
227	
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229	
25	
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230	
35	
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234	
45	
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236	
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238	
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241	
70	
242	
75	

FORMULAE OF PROTOTYPE NUMBERS

Prototype number	Formula
244.....	
253.....	
107.....	A physical mixture of and

We claim:

1. A storage-stable, oil-in-water type emulsion comprising water, an anionic surface-active emulsifying agent, and as the internal phase, a lower alkyl ester of a carbocyclic aromatic monocarboxylic acid having not more than two carbocyclic rings, the weight ratio of said emulsifying agent to said ester being from about 1:50 to 1:2.

2. An emulsion according to claim 1 in which said ester is methyl salicylate.

3. An emulsion according to claim 1 in which there is also present a finite amount of non-ionic surface-active emulsifying agent, the ratio of the total weight of said emulsifying agents to said ester not exceeding 1:2.

4. An emulsion according to claim 3 in which said ester is methyl salicylate.

5. A liquid composition characterized by the ability to form a storage-stable, oil-in-water type emulsion when stirred in water, said liquid composition comprising from

about two to about fifty parts by weight of a lower alkyl ester of a carbocyclic aromatic monocarboxylic acid having not more than two carbocyclic rings, said ester having dissolved therein about one part by weight of an emulsifying agent comprising an anionic surface active material.

6. A composition according to claim 5 in which said emulsifying agent also includes a finite weight of a non-ionic surface active material.

7. A method capable of level dyeing a hydrophobic synthetic fiber without prepadding which comprises, forming a storage-stable, oil-in-water type emulsion comprising water, an anionic surface-active emulsifying agent, and as the internal phase, a lower alkyl ester of a carbocyclic aromatic monocarboxylic acid having not more than two carbocyclic rings, the weight ratio of said emulsifying agent to said ester being from about 1:50 to 1:2; combining a minor amount of resultant storage-stable emulsion and a major amount of an aqueous medium containing a dye capable of dyeing said fibers, whereby an extended emulsion is formed; and then, at a temperature between about 160° F. and about the boiling point of said extended emulsion, treating said fibers with said extended emulsion, whereby said emulsion is broken and level dyeing of said fibers is obtained.

8. A process according to claim 7 in which said fiber is a polyglycol terephthalate.

9. A process according to claim 7 in which said emulsifying agent also includes a finite weight of a non-ionic surface active material.

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