The present invention relates to improved methods of dyeing hydrophobic, synthetic organic materials in the form of fibers, fabrics and shaped articles, and to novel compositions for use therein.

Within recent years, the number of synthetic materials, especially in fiber form, which have been developed and offered for commercial acceptance has increased many fold. Typical of such materials are the polyester fibers, such as "Dacron," "Kodel," "Vyon," "Terylene" and "Teron"; the cellulose triacetate fibers such as "Acril" and "Triec"; the acrylic fibers such as "Acrylic" and "Creslan"; and so forth.

Such hydrophobic materials cannot be satisfactorily dyed by the ordinary dyeing procedures previously used for dyeing cotton, wool, silk, regenerated cellulose, and the like. When such ordinary dyeing procedures are used for dyeing hydrophobic synthetic organic materials, the dye does not penetrate the materials and either no dyeing is obtained or, if some measure of dyeing is obtained, the color is not fast and washes out of the materials. As a result, the dyeing of such hydrophobic materials is presently effected by other methods such as, for example, by being carried out in the presence of a swelling agent which forms or opens the pores of the hydrophobic materials and permits the dye to enter and remain there in a color-fast manner.

Very many chemical compounds and compositions have been developed as assistants or carriers for the dyeing of hydrophobic materials. Many of these are phenols or phenolic derivatives which are acidic in nature and consequently are not completely satisfactory or acceptable to industry. Additionally, these phenolics decrease light fastness and introduce persistent objectionable odors during the dyeing process which often remain in the dyed materials after dyeing. Other dyeing carrier compositions have also been toxic of irritating, or have been expensive and uneconomical, and accordingly also are not completely satisfactory or acceptable to industry.

Another objectionable feature of prior art carriers is noted in that in many cases, when it was desired to make additions either of more dye or more dyeing carrier to heated dyeing compositions during dyeing operations, in order to obtain or match various shades, it was necessary to cool the heated dyeing composition before such additions could be made. Such cooling and subsequent reheating to dyeing temperatures to resume dyeing operations was time consuming and costly and consequently objectionable.

A newly developed carrier composition has now been discovered and developed which is non-phenolic in nature, is not toxic or irritating, has excellent light fastness, and does not introduce any objectionable odors during dyeing or subsequent use. Furthermore, additions may be made to heated dyeing compositions containing such a carrier at elevated temperatures without cooling, as previously required.

Such an improved dyeing carrier composition comprises trichlorobenzene and a select combination of emulsifying agents which are employed in specified proportions with respect to one another and to the trichlorobenzene whereby the desired abovementioned results are obtained. The term "trichlorobenzene," as used herein, is intended to cover any one of the isomeric forms of trichlorobenzene, or any combination or mixture of the same in any proportion. 1,2,3-trichlorobenzene (vic-trichlorobenzene) and 1,2,4-trichlorobenzene (sym-trichlorobenzene), and especially mixtures of the same, are preferred due to the ready commercial availability thereof but such is not intended to exclude the use of 1,3,5-trichlorobenzene (sym-trichlorobenzene).

The select combination of emulsifying agents comprises, as a first ingredient, a monovalent salt of a sulfated alkyl polyether alcohol. Such an emulsifying agent is obtained by treating a long chain aliphatic alcohol containing from 8 to 14 carbon atoms, and preferably from 10 to 14 carbon atoms, with an alkylene oxide, preferably ethylene oxide, and then treating the resulting alkyl polyether alcohol with concentrated sulfuric or sulfamic acid to sulfate the same, and subsequently neutralizing the sulfated alkyl polyether alcohol to yield the desired emulsifying agent.

The long chain aliphatic alcohol containing from 8 to 18 and preferably from 10 to 14 carbon atoms may possess a relatively straight alkyl chain such as when derived from nut oils. Coconut, babassu, and palm kernel oil having a low iodine value and containing a high percentage of almost 50% saturated twelve carbon atom alcohols and a substantial percentage of saturated fourteen carbon atom alcohols are particularly applicable. Other oils suitable for the purposes of the present invention are coconut oil, oiticica oil, murumuru oil, and tucum oil. The mixture of isomeric, highly branched chain tridecyl alcohols such as obtained by the exx process is similarly particularly applicable.

The extent of the treatment of the alcohol with ethylene oxide may be varied within relatively wide limits depending upon the degree of the hydrophilic properties desired. The "Emulsifine" series of nonionic emulsifiers are examples of such alkyl polyoxyethylenoxy alcohols wherein the degree of hydrophilic properties is increased as the number of moles of ethylene oxide incorporated in the alcohol is increased. For the purposes of the present invention, the introduction of from about 2 to about 30 moles of ethylene oxide in the alcohol has been found satisfactory, with from about 3 to about 10 moles being preferred.

The alkyl polyoxyethylenoxy alcohols are then sulfonated (actually sulfated) by treatment with concentrated sulfamic or sulfuric acid by procedures well known to industry.

Subsequent to the treatment of the alkyl polyoxyethylenoxy alcohol with the sulfamic or sulfuric acid, neutralization is effected by treatment with a base, such as ammonia or an alkali metal hydroxide or carbonate, or the like. As a consequence, the final emulsifier is a monovalent salt of a strong acid, is more resistant to hard water, and is more stable in aqueous solutions of low pH.

The second ingredient of the select combination of emulsifying agents is obtained by treating an unsaturated animal, fish or vegetable fat or oil, preferably tallow, sperm oil or castor oil, with a sulfating agent such as sulfuric or sulfamic acid. The resulting product, although frequently referred to as sulfonated is actually sulfated and contains the —OSO₂H radical or a salt thereof, such as the ammonium salt, i.e., —OSO₂NH₄. Although sulfonated tallow, sperm oil and castor oil are used in describing the applicability of the present invention, it is to be appreciated that other sulfonated animal, fish or vegetable fats or oils are utilizable. Illustrative of other unsaturated fats and oils suitable for use in the present inventive concept are peanut oil; rape (rapeseed) oil; olive oil; palm oil; neat's foot oil; teeseed oil; almond oil; apricot kernel oil; etc.

As used herein, the term "animal" naturally refers to...
land animals and the term "fish" is intended to indicate a marine origin and includes aquatic mammals, notably the whale.

As used herein, the term "unsaturated" fat or oil is intended to cover those fats or oils containing at least about 40% by weight of unsaturated monoenoic acids, notably oleic acid, and normally greater than about 60% by weight of unsaturated monoenoic acids. Such unsaturated fats and oils have iodine values in excess of about 30, and often in excess of about 80, but not substantially in excess of about 115, at which point their drying characteristics, due usually to the presence of higher percentages of monoenoic acids, notably linoleic acid, would begin to interfere with the application of the present inventive concept. Modified fats and oils, for example, those prepared by hydrogenation processes, are suitable for the purposes of the present invention provided their properties and characteristics are as described herein.

In the dyeing carrier compositions, the ranges of the relative proportions of the trichlorobenzene, the monovalent salt of the sulfated alkyl polyether alcohol, and the sulfonated animal, fish or vegetable fat or oil may be varied within relatively wide limits. For example, the dyeing carrier composition may comprise from about 40 parts to about 80 parts by weight of the trichlorobenzene, from about 2 parts to about 30 parts by weight of the monovalent salt of the sulfated alkyl polyether alcohol, and from about 6 parts to about 40 parts by weight of the sulfonated animal, fish, or vegetable fat or oil.

The amount of the dyeing carrier composition to be added to the dye bath may be varied within relatively wide limits and depends primarily upon the dry weight of the hydrophobic synthetic materials being dyed. Within the broader aspects of the present invention, from about 1% to about 12% by weight of the dyeing carrier, based on the dry weight of the hydrophobic synthetic materials, has been found satisfactory. Within the more commercial aspects of the present invention, from about 11% to about 10% has been found preferable, with optimum values being noted in the range of from about 2% to about 8% by weight.

The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

Example I

The dyeing carrier is prepared from: 65 parts by weight of trichlorobenzene (technical grade, mixture of 1,2,4- and 1,2,3-trichlorobenzene, with 1,2,4- predominating); 15 parts by weight of the ammonium salt of sulfated tridecyl polyethyleneoxy ethanol (60% active); and 20 parts by weight of sulfonated castor oil (75% concentrated solution). Analysis of the alcohol reveals the treatment with about 4 moles of ethylene oxide. The castor oil used analyzes 0.3% stearic acid, 8.0% oleic acid, 87.8% ricinoleic acid, and 3.6% linoleic acid. Its iodine value is 85.

The resulting product is a light amber-colored liquid which is self-dispersible in warm water and is compatible with anionic dyeing assistants, detergents and sequences. Its pH (1% solution) is neutral and it has excellent storage stability and "shelf-life." The dyeing carrier is dispersed in water at 160 °F. (71 °C.) and is thoroughly stirred to yield a milk-blue colored stable emulsion. A fabric woven from "Dacron" polyester fibers is prepared for dyeing by thorough scouring and cleaning to remove lay marks, oxidized stains and other soil. The fabric goods are soaked in and a small amount (about 0.1% of the anionic dyeing assistant and enough sequestering agent (tetra sodium salt of ethylene diamine tetra acetic acid) is added to soften the water. The temperature of the bath is raised to 120 °F. (49 °C.). The dyeing carrier is run into the dye bath in an amount equal to 7%, based on the dry weight of the "Dacron" polyester fabric, with the temperature of the bath being maintained at 120 °F. (49 °C.). The dye is then added in the amount desired and the temperature of the bath is raised close to the boil and maintained at that temperature until the desired shade is obtained. The dyed goods are rinsed in water at 130 °F. (54 °C.). No objectionable, irritating or toxic odors are noticed at any time during the dyeing process. The dyeing carrier promotes deep penetration of the dye and prevents bleeding on wet pressing and processing. The dyeing is uniform and level. No objectionable, irritating or toxic odors are developed during subsequent use of the dyed fabric. Its light fastness is excellent.

Example II

The procedures of Example I are followed substantially as set forth therein except that the amount of the dye is deliberately reduced so that it is insufficient to yield the desired shade when the dye bath is brought close to the boil. An additional amount of dye is added, without cooling the dye bath, and the desired shade is obtained. The properties of the dyed fabric are similar to those obtained in the dyed fabric of Example I.

Example III

The procedures of Example I are followed substantially as set forth therein except that a fabric woven from "Acrilan" acrylic fibers is used. The amount of dyeing carrier used is reduced to 4%, based on the dry weight of the fabric. The results are satisfactory and are comparable to the results obtained in Example I.

Example IV

The procedures of Example I are followed substantially as set forth therein except that a fabric woven from "Arnell" cellulose triacetate fibers is used. The amount of dyeing carrier used is reduced to 2%, based on the dry weight of the fabric. The results are satisfactory and are comparable to the results obtained in Example I.

Example V

The procedures of Example I are followed substantially as set forth therein except that the percentage of the constituents of the dyeing carrier is changed to: 40 parts by weight of trichlorobenzene; 5 parts by weight of the sodium salt of sulfated tridecyl polyethyleneoxy ethanol (60% active); and 10 parts by weight of sulfonated castor oil (75%). About 8% by weight of this carrier is used, based on the dry weight of the fabric being dyed. The results are satisfactory and are comparable to those obtained in Example I.

Example VI

The procedures of Example I are followed substantially as set forth therein except that the percentage of the constituents of the dyeing carrier is changed to: 80 parts by weight of trichlorobenzene; 25 parts by weight of the sodium salt of sulfated tridecyl polyethyleneoxy ethanol (60% active); and 40 parts by weight of sulfonated castor oil (75%). About 5% by weight of this carrier is used, based on the dry weight of the fabric being dyed. The results are satisfactory and are comparable to those obtained in Example I.
Example VII

The procedures of Example I are followed substantially as set forth therein except that sulfonated sperm oil is used to replace the sulfonated castor oil. The sperm oil, prior to its treatment with the concentrated sulfuric acid, analyzes 8.0% myristic acid, 12.1% palmitic acid, 2.3% stearic acid, 1.5% C14-unstaturated acid, 15.0% palmi- toleic acid, 33.4% oleic acid, 18.7% C16 and C18-unstaturated acids, and 9% linoleic acid. Its iodine value is 110. The dyeing carrier is self-emulsifiable in water and yields a uniform stable emulsion.

Example VIII

The procedures of Example I are followed substantially as set forth therein except that the ammonium salt of sulfated tridecyl polyethyleneoxy ethanol is replaced by the ammonium salt of sulfated lauryl polyethyleneoxy alcohol (also 60% active). Lauryl alcohol is the starting alcohols; about 4 moles of ethylene oxide are added to the alcohol nucleus; and sulfamic acid is the sulfonating agent. The dyeing carrier disperses easily in water and yields a stable emulsion.

Example IX

The procedures of Example I are followed substantially as set forth therein except that sulfonated beef tallow is used to replace the sulfonated castor oil. The beef tallow, prior to its sulfonation with concentrated sulfuric acid, analyzes 0.2% lauric acid, 3.1% myristic acid, 24.9% palmitic acid, 24.1% stearic acid, 41.8% oleic acid, 2.4% palmitoleic acid, and 1.8% lino-leic acid. Its iodine value is 44. The dyeing carrier is readily self-dispersible in water and yields a uniform stable emulsion.

Although several specific examples of the inventive concept have been described, the same should not be con- strued as limited thereby nor to the specific features men- tioned therein but to include various other equivalent features as set forth in the claims appended hereto. It is understood that any suitable changes, modifications and variations may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts of a member of the group consisting of sulfonated animal, fish and vegetable fats and oils, and mixtures thereof.

2. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts thereof.

3. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts of a sulfonated tallow.

4. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts of a sulfonated fish oil.

5. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts of a sulfonated sperm oil.

6. A dyeing carrier for use in dyeing hydrophobic, synthetic organic materials comprising from about 40 to about 80 parts by weight of trichlorobenzene, from about 2 parts to about 30 parts by weight of a water soluble monovalent salt of a sulfated alkyl polyether alcohol derived from a long chain aliphatic alcohol containing from 8 to 18 carbon atoms, and from about 6 parts to about 40 parts of a sulfonated castor oil.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,057,674

David M. Musser et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 44, for "of" read -- or --; line 71, for "th" read -- the --; column 5, line 31, for "linoleic" read -- linoleic --; column 6, lines 34 and 37, for "above" each occurrence, read -- about --.

Signed and sealed this 26th day of March 1963.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents