

UNITED STATES PATENT OFFICE

2,042,473

DYE PREPARATION

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No Drawing. Application December 9, 1932,
Serial No. 646,496

10 Claims. (Cl. 8-6)

My invention relates to an improved packaged dye for home use and the method of producing the same.

It is well understood that the art of dyeing fabrics is an exceedingly complicated and technical business. Regularly established dyeing industries are equipped to make use of all of the known chemicals, assistants, mordants and the like which the industry possesses; as well as all of the equipment for turning out a first class result independent of the type of material or color. The home dyer has none of the facilities available to the regular dyeing establishments and so a dye must be placed in his hands which, with the limited experience and ability available to the amateur dyer, will turn out a first class product on all types of materials. The development of a dye for home use, therefore, is an exceedingly technical problem because the dye must have characteristics which the skilled dyer would never expect in his own product.

There has been an extensive development of dyes for home use. The so called soap dyes were one of the early developments along this line. These took on different forms, all attempting to improve the product. The soap dyes have employed assistants with them such as sulphonated oils and other materials along this general line. Besides taking a considerably long time to dissolve, they possessed other disadvantages at times, well known to those skilled in the art. Applicant's prior Patent No. 1,752,184 represented a development which was a great step forward in the art and consisted of substituting for the soap in the soap dye a material which would function as a soap in its desirable properties but which would avoid the disadvantages attending the use of soap. The resulting product had excellent solubility, proper leveling; it did not precipitate out in the presence of hard water as soap did. The principal disadvantage of this product, however, was that after dyeing with it the garments did not have the proper finish and the proper "feel". In other words, the garment so dyed did not have the appearance of a new garment, which is one of the features expected in a newly dyed piece of fabric. It is well known that this finish and feel can be obtained in part from the use of an oleaginous material in the dye bath, such as a sulphonated oil or similar oleaginous substance, it being known that the more oleaginous the product, the greater the improvement insofar as the finish and feel. I attempted to improve the dye product produced in accordance with the above mentioned patent by employing

a mixture of sulphonated alkylated polynuclear hydrocarbons and the compound having fatty properties such as sulphonated oil or a sulphonated soap. I found that this was impossible in a practical way because the presence of the oily material seemed to deprive the product of the desirable characteristics obtained by the use of the wetting agent. In other words, the resulting dye no longer dissolved readily and possessed some of the same disadvantages attending the use of ordinary soap dyes. In spite of all of the developments, I still found that there was difficulty due to the forming of lime salts and the disadvantage of not being able to work in a slightly acid medium, which is preferable for most dyeing. With this knowledge of the art before me, it was my object to produce an improved dye for home use which would have all of the advantages of such dyes heretofore used but would also avoid all of the disadvantages thereof.

Another object is the provision of an improved dye for home use adapted to be employed with different types of fabrics.

Another object is to place a packaged dye in the hands of the ordinary housewife which will permit her substantially to duplicate the results obtained in the most up-to-date dyeing establishments.

Other objects and features of the invention will be apparent as the detailed description progresses.

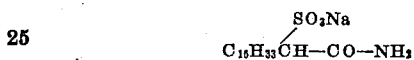
In developing my improved product, I proceeded on the assumption that the carboxyl group in some of the compounds, soaps, sulphonated oil, etc., employed in home dyes was undesirable, for the reason that it forms insoluble precipitates with calcium and magnesium salts found in hard water. This was not a new concept as I knew that considerable work had been done either to replace the carboxyl group with another group or to combine it chemically with some other compound or compounds so that it would not exert its harmful effect. In sulphonated oils, the carboxyl group is in the form of a glyceride, but being a tri-glyceride, the ratio of the esterifying alcohol to the total amount of the carboxyl groups is not sufficient to keep it stable and for this reason when heated with water it hydrolyzes and forms lime salts and insoluble greases. A great advance was made by the realization that when the carboxyl group is esterified with a monovalent or polyvalent alcohol or amidized with ammonia or an amine or their substitution products, the resulting products become stable. In the case of the polyvalent alcohols, not all the

valences are esterified with the carboxyl groups and at least one hydroxy group is left either free or positively substituted. The compounds obtained are quite stable and surprisingly also excellent wetting agents and I have found that compounds of this kind have all the desirable properties when employed with a dye for home use without having to use additional wetting agents of the type required previously.

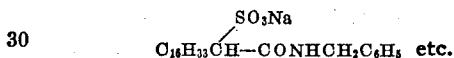
To describe such compounds, I wish to cite the following references: Monovalent alcohol esters of a sulphonated oil are the butyl ester or benzyl ester of sulphonated oleic acid as described in the United States Patent No. 1,822,977, Example Three; two other Patents 1,822,978 and 1,822,979 describe similar compounds and methods of making them. These compounds can be made by esterifying a sulphonated fatty acid or by sulphonating an esterified fatty acid which is esterified with a monovalent alcohol.

Amids of sulphonated fatty acids can be characterized by the following compounds:

(a) Sulphonated stearyl amid of the formula—



and the alkyl and aryl substitution product thereof like benzyl stearyl amid sulphonic acid



(b) Sulpholeil amid of the formula—



In the case where divalent alcohols are used like ethylene glycol, diethylene glycol or trivalent alcohol like glycerol, then at least one of the hydroxy groups should remain free or positively substituted and preferably two. In other words, if sulpholeic acid is esterified with ethylene glycol, diethylene glycol or glycerol leaving one of the hydroxy groups of the glycol free or positively substituted or one or two of the hydroxy groups of glycerol free or positively substituted, desirable compounds are obtained. These compounds can also be made by first esterifying the fatty acid and making compounds like monostearyl glycol or monooleyl glycol or monostearyl glycerol or distearyl glycerol and then sulphonating the ester where the sulphuric acid group will go into the fatty acid nucleus or preferably form an ester with the hydroxy group. Phosphoric acid esters can be made which are just as efficient. To illustrate, I wish to refer to German Patent No. 193,189 where the distearyl glycerol phosphoric acid ester is described. Another compound belonging to the same class is the mono-oleyl ethylene glycol sulphonated as described in French Patent No. 721,340, Example 1.

The compounds described in the above paragraph are esters of alcohols and sulphuric or phosphoric acid. An advance in this was made in the United States Patent No. 1,881,172 in which case the acidic group is tied directly to the carbon atom of the esterified alcohol giving a sulphonic acid group. In this case fatty acid esters of ethane sulphonic acid are obtained of the general formula—



In other words, fatty acid products of ethionic acid are obtained. Those compounds have all the desirable properties like wetting, stability in lime water and slightly acid solutions and also give the proper finish to textiles.

Along with the line of development of making

the carboxyl group harmless through esterification or amidization, another method was devised which is proving to be commercially very successful and scientifically correct, viz: the carboxyl group is reduced to an alcoholic group and the corresponding alcohol sulphated or phosphated.

In the industry, lauric acid has been successfully reduced to form the lauryl alcohol, stearic acid to form the stearyl alcohol, oleic acid to form the oleyl alcohol. Cetyl alcohol is, of course, a natural product being obtained from the saponification of spermaceti.

Any one of these alcohols can be properly sulphated or phosphated to form the sulphuric or phosphoric acid esters of the corresponding alcohols. Those esters and their water soluble salts are excellent penetrating agents, emulsifying agents, and also finishing materials. They are known in commerce under the name of "Gardinols", "Avirols", etc.

The development in the last line of work has brought back to life another class of substances which, from the viewpoint of the chemical and physical action, replace soap with great advantage but were never considered commercially in view of the fact that the matter of preparation was too involved and they could not be obtained in either commercial quantities nor at prices in which they could be serious competitors to soap. I am referring in this case to the straight sulphonic acid of aliphatic hydrocarbons having a chain of eight carbon atoms or more. A representative of this class is cetyl sulphonic acid and its salts which were described in great detail by Reyehler in the *Kolloidale Zeitschrift*, volume 12, page 277, in 1913. This compound is very soluble in water in the form of its free acid or salts, gives an excellent foam, penetrates well, and has fatty characteristics. It was of no commercial value until lately and Prof. Schrauth has published an article in the *Chemiker Zeitung* for 1931, page 1984, in which he states that when sulphuric esters of aliphatic alcohols are treated with sodium sulphite, the sulphonic acids of the corresponding hydrocarbons can be obtained in good commercial quantities. This work was further followed up and described in English Patent No. 358,583, in which case unsaturated hydrocarbons with a chain of not less than eight carbon atoms are sulphonated, in which case true sulphonic acids are formed and the next carbon to the carbon that has the sulphonic acid group on it has a hydroxy group. As one product I can quote the hydroxy octadecyl sulphonic acid of the formula—



which was described in Example One of the above named patent. While all those above named chemicals will fall into a certain number of chemical groups depending upon their structure, yet from the viewpoint of the physical behavior, especially in regard to my application of them, they are all to be construed as one class.

Chemically we may say those substances are either sulphonic or phosphonic derivatives of long chain aliphatic hydrocarbons or they are sulphuric or phosphoric acid esters or for that matter esters of oxygenated inorganic acids of long chain aliphatic alcohols; or sulphuric or phosphoric acid derivatives or for that matter derivatives of oxygenated inorganic acids of amids of higher aliphatic fatty acids and their derivatives or esters of higher aliphatic acids esterified in the carboxyl group either with monovalent al-

cohols or polyvalent alcohols in which not all of the hydroxy groups are esterified with carboxylic acids.

On the other hand, from a physical viewpoint and from a viewpoint of application, they have the following in common:—They are chemicals having polar and non-polar groups connected together in the same molecule in a very balanced ratio in which the non-polar group is strongly oleophilic due to the fact that it has a chain of at least eight carbon atoms or more and has affinity for fats, oils, or different organic compounds. The polar group is a strong oxygenated inorganic acid that makes the compound as a whole strongly hydrophilic, makes the compound easily soluble in water and thereby the whole compound as such becomes a very good penetrating agent, an ideal emulsifier, being in a position to disperse fats and greases in water and give a "fatty feel" to compounds with which it is penetrated from a purely water medium.

In the above description I have given an idea of the different classes of compounds and representative examples that are suitable for my purpose. I have done it only for the purpose of teaching the art to the extent where it would be easy for any qualified chemist to arrive at other classes of the same general characteristics.

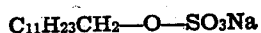
In general, I found that the proper types of compounds that are necessary for my purpose must be quite soluble by forming a true solution or colloidal solution or form at least a very fine stable dispersion in water without precipitating with other agents under any condition in which they may be used. In other words, the compound employed must be strongly hydrophilic and have great penetrating value but at the same time it must also possess oleophilic properties to the point where it will be a good "finishing" agent, leaving the textile material treated pliable with a soft "feel". Any compound answering this description will naturally fall within my disclosure.

It is understood that also solvents, diluents, fillers, and other assistants may be used without departing from the true scope of the invention.

The following examples are illustrative of my invention:

Example 1

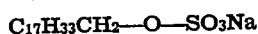
Per cent
20 direct black, color index CI #581
50 10 of the sodium salt of the sulphuric ester of lauryl alcohol of the general formula



commercially known as Gardinol WA
55 70 common salt.

Example 2

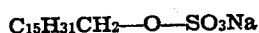
Per cent
5 of cyanone blue 5R, color index #289
5 direct blue BB, color index #406
60 90 of the sodium salt of the sulphuric acid ester of oleyl alcohol of the general formula



otherwise known as Gardinol CA
65

Example 3

Per cent
25 of direct green, color index #593
5 of chrysophenin, index #365
70 25 of the sodium salt of the sulphuric acid ester of cetyl alcohol of the general formula



otherwise known as Avirol 142
75 45 ammonium sulphate

Example 4

Per cent
3 of methylene blue, color index #922
3 of sodium salt of the sulphuric acid ester of reduced coconut oil fatty acids, commercially known as Gardinol R
94 dextrine

Example 5

Per cent
5 acid rhodamine 3R, Manual 534
5 sodium cetyl sulphonate
45 alcohol
45 glycerin

Example 6

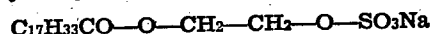
Per cent
20 Catechu G N, color index 420
3 hydroxy-octadecyl-sulphonic acid, general formula



77 ammonium sulphate

Example 7

Percent
30 alizarine blue, color index #1054
15 sodium salt of the sulfation product mono-oleyl ethylene glycol of the formula



55 common salt

Example 8

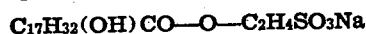
Percent
5 of cyanone blue 5R, color index #289
5 direct blue BB, color index #406
15 of the sodium salt of the sulphuric acid ester of oleyl alcohol of the general formula



otherwise known as Gardinol CA
75 of Glauber salt

Example 9

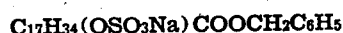
Percent
10 pontamine bordeaux B, color index #375
9 cyanine blue 5R, color index #289
20 dark blue BH, color index #401
11 sodium salt of ricinoleic acid of ethionic acid of the general formula



50 Glauber salt

Example 10

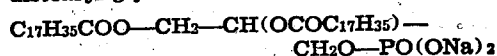
Percent
20 algal scarlet G, color index #1129
20 benzyl ester of sulpholeic acid of the general formula



10 of sodium hydroxide
20 of sodium hydrosulphite
30 of sodium carbonate

Example 11

Percent
10 of lithol rubin BN, color index #163
10 of the salt of the phosphoric acid ester of distearyl glycerin of the formula



10 soda ash
70 Glauber salt

Example 12

Percent
10 chrysamine, C. I. 365
10 of sulphonated oleyl amide of the general formula $C_{17}H_{34}(OSO_3Na)CONH_2$
80 salt

Example 13

Percent
 10 pontamine bordeaux B, color index #375
 10 lecithin
 5 20 salt
 60 sugar.

My preparation may be in either solid, liquid, or paste form, using diluents, fillers, or assistants of various kinds. The penetrating chemicals must have a very strong hydrophilic group such as a strongly acidic group, like sulphonic acid group, phosphoric acid group or similar groups. They must have an excellent wetting out action, should preferably dissolve completely in water, make true or colloidal solutions or at least disperse completely to form stable dispersions. They must also have properties that will give the article with which they are distributed stability and give it some oily "feel" which is accomplished by these particular chemicals having an alkyl group of not less than eight carbon atoms or its derivatives like hydroxy, halogen derivatives, acidic derivatives. They also may have an aralkyl group, the alkyl group still not having less than seven carbon atoms.

It will be noted that this general formula will take in any of the compounds discussed previously in the specification and define it to the point where everyone skilled in the art will be able to use it as a guide for his work.

The degree of the oleophilic properties of these compounds can be regulated by the length of the hydrocarbon chain. Those from C_8 up to C_{12} have the oleophilic properties not as pronounced as those beginning with C_{16} , and depending upon the desirability of the degree of oiliness required those compounds can be chosen to suit the product, but it must be understood that in no case can the product be useful unless it is still quite hydrophilic.

In describing the invention, it is understood that the examples and illustrations given are to be taken in a descriptive sense rather than in a limiting sense. As far as the specific examples of the dye products are concerned, these are meant to show different types of wetting and combining agents expressed by the general formula.

I have referred hereinabove to the solubility of the class of chemicals which I employ by stating that they should be freely soluble, colloidal soluble or form very fine dispersions in aqueous media. The terms "soluble" and "solubility" as employed in the claims, therefore, are used in the broadest sense to refer either to true solutions or to colloidal solutions or very fine dispersions which as far as my purpose is concerned have substantially the same function as true solutions. It should also be borne in mind that many terms employed in the specification are used in a descriptive sense rather than in a limiting sense and the details are given for illustration so that those skilled in the art may be able to practice the invention. The novelty is defined in the appended claims. "Water soluble" as employed in the claims is used in a broad sense to include the characteristics of either molecular or colloidal dispersibility.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and an inorganic oxygenated acid ester of an aliphatic alcohol having a chain of not less than eight carbon atoms, said dye

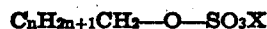
composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

2. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and a salt of an inorganic oxygenated acid ester of an aliphatic alcohol having a chain of not less than eight carbon atoms, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

3. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and a sulphuric acid ester of an aliphatic alcohol having a chain of not less than eight carbon atoms, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

4. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and a salt of a sulphuric acid ester of an aliphatic alcohol having a chain of not less than eight carbon atoms, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

5. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and a salt having the general formula—



wherein "n" is a whole number, at least seven, and "X" is a cation, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

6. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and the sulphuric acid ester of lauryl alcohol, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

7. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and the sodium salt of the sulphuric acid ester of lauryl alcohol, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

8. A home dye composition in solid form comprising an intimate admixture of a water-soluble dye and a salt of the sulphuric acid ester of oleyl alcohol, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

9. A home dye composition in solid form comprising an intimate admixture of a normally water-soluble dye and an inorganic oxygenated acid ester of cetyl alcohol, said dye composition

possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations.

5 10. A home dye composition in substantially solid form comprising an intimate admixture of a normally water-soluble dye and a sulphuric acid ester of oleyl alcohol wherein the sulphuric

acid group is esterified with the hydroxy group of the oleyl alcohol, said dye composition possessing the properties of imparting an "oily" feel to fabrics dyed therewith and producing even, level shades under any of the conditions normally encountered in home dyeing operations. 5

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