is rapid and we believe very positive.

We have found that it is difficult to judge the initial color of fat carrying green when liquid by the Lovibond color, even with blue glasses or by the F.A.C. color tubes. It is even more difficult to judge the color of the copper treated fats in the liquid phase. Variations to the extent of a considerable quantity of green are not detectable when the fat is liquid. When the fat is chilled quickly, variations in green are much more readily detected. If standards are to be made, they will probably be of the Munsell-paper type and for solid fats.

We will show a series of samples to indicate the nature and application of the test. To show how chlorophyll may be extracted by a fat, a small amount of spinach was cooked in a very small amount of water. It was then mixed with neutral liquid petrolatum. After the extraction was made, sufficient white paraffin was added to solidify the petrolatum at room temperature. You will note that the petrolatum extract, while greenish in hue, carries considerable yellow. The petrolatum extract, when given the copper treatment, becomes very decidedly green.

Some pure rendered leaf lard was used to extract a mixture of alfalfa and spinach. Here, again, in addition to chlorophyll there is considerable yellow coloring material extracted. When the lard chlorophyll extract is given the copper treatment, the intensity of the green is very much increased. Some of the lard extract was saponified into soap which you note is also very green. The lard itself is white, shows no green on the copper test and produces very white soap.

In addition to these synthetic samples, we wish to show a representative series of a few sets consisting of the untreated raw tallow, the tallow after copper treatment, and the neat soap made in glass from the raw tallow. These have been selected from a large number of such sets which we have made. These tallows were all portions of actual shipments.

These samples cover a range from light tallows to the darker grades. Some give a decided green color on copper treatment while others of about the same raw color do not produce a green color with copper. We wish to call your attention to some of the deep yellow samples which would not be selected as green except by those familiar with the soaps from such tallows. Many of these "golden" tallows turn to deep green on the copper test, and produce green soap. We want particularly to call attention to how closely the colors of all the copper treated stocks correlate with the colors of the neat soaps from the corresponding raw stocks.

It is obvious that fats rendered in copper equipment will not respond to the test, for if chlorophyll is present in such fats, the green color will be at a maximum. Tallows of this type will be so green that there will be little doubt as to their greenness. We are showing a sample of such a tallow which did not respond to the test. Possibly it could not be any greener. Analysis showed that it contains as received 8.5 p.p.m. of copper. Since this paper was written, the producer of this tallow has informed us that the tallow was extracted tallow from which the solvent was evaporated in copper equipment. Soap made from this tallow is deep green.

Naturally, the question will be raised whether the increase in green color on heating in the presence of copper is not due to the formation of copper soap by the fatty acids. In reply to this, you will note that those tallows which did not produce green neat soap did not show green when heated with copper, although each contained some free fatty acid. The petrolatum chlorophyll extract showed the typical copper reaction. In addition, tallow fatty acids and light commercial red oil all give negative results on the copper treatment.

It is possible that the increase in the intensity of the green color is not entirely due to the formation of a copper chlorophyll. It may be due, in part, to a change in the coloring power of the yellows and reds so that after the test the green is more prominent. Regardless of the explanation, we are sure that the test is positive and one of value that may be carried out by the shipper, the purchaser, or the broker very rapidly and with relatively simple equipment.

H. B. STEVENSON.
C. P. LONG.

The Procter & Gamble Co.,
Ivorydale, Ohio.
October 5, 1934.

THE RELATION OF SULPHONATED COMPOUNDS TO THE TEXTILE INDUSTRY

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A Paper Delivered Before the 8th Fall Meeting—A.O.C.S.

Any compound which is used by millions of pounds annually is of interest not only to the manufacturers but also to the users. In the bulletin, "Census of Manufacturers, 1931" on "Natural Dyestuffs, Mordants and Assistants, and Sizes," appear the following figures: under the heading of Assistants 1929, is Turkey Red Oil 24,260,000 pounds, softeners 31,612,775 pounds, other assistants were not noted in pounds but were given a value of $2,103,171. Then under the year 1931, we find Turkey Red Oil 13,549,539 pounds, softeners 33,111,163 pounds, other assistants of a value of $2,458,737.

Then from Approved Code No. 469 of the Sulphonated Oil Manufacturing Industry, we quote the following: "It is recognized that there are a larger number of firms which may intermittently manufacture sulphonated oil products but there are considered to be essentially about fifty bona-fide members of the Industry. The Industry reported that the aggregate invested capital in 1928 amounted to $4,227,526, and in 1933 this was increased to $5,973,578. The aggregate annual sales of production in 1928 is purported to have been $9,614,975, and in 1933 was $12,838,800."

From the above figures it is easily seen that much sulphonated oil and sulphonated compounds are used. Of the above amount, the leather industry used a great deal, but also there is coming more and more in the textile industry, the use of not only sulphonated oil (the old Turkey Red oil), but also the newer sulphonated compounds. This paper will deal with the compounds in relation to the textile industry.

As oil chemists, you all are doubtless familiar with the process whereby vegetable oils have been treated with sulphuric acid to make the sulphonated product. You all are likewise aware of the fact that the insoluble oil becomes a compound which is soluble in water. Both castor and olive oil have been sulphonated for many years, but the manufacturers also sulphonated other oils such as neatsfoot, linseed, rape, tallow, cottonseed, etc. Dyers, printers, mercerizers and finishers of the textile industry all realize that the different compounds have certain characteristics which are of special value in certain processes.

The regular sulphonated oils are often used as bases for solvents and penetrating agents which themselves are not soluble or miscible with water when used alone.

There is a limit to the amount of sulphonation possible with vegetable oils, and as a high degree of sulphonation makes a more soluble compound, there have been placed on the market other sulphonated compounds of higher SO_3 content such as the oleo, palmito and glyceryl sulphates.

Then there are the napthalene sulphonic compounds which have found much use as wetting-out agents. There are compounds of the sodium tetralin sulfonate type which are recommended as dispersing agents. We also have the compounds such as Gardinol, Igepon, Avirol, etc., of the sulphonated fatty alcohol type, and these are now of much importance.

We find the Mapro compounds, another type of sulphonated alcohols being used for dispersing, wetting-out, penetration and finishing agents.

Chemical and Physical Properties of the Fibres

The four fibres mostly used in textiles are cotton, wool, silk and rayon; all of which differ from each other physically and chemically. First taking up cotton, we know that it is composed chemically of carbon, hydrogen and oxygen in the form of cellulose. This is the same as in the regenerated cellulose compounds called rayon, but the arrangement of the molecules is evidently different as we do not get exactly the same reactions with the dyestuffs. As to physical properties, there is much difference, not only in the appearance, but also in the impurities present. Raw cotton is protected by the presence of a waxy substance which prevents the cotton in the field from becoming wet during rain storms. This waxy substance naturally resists the action of the solutions used in scouring, bleaching and dyeing unless it is removed. Here is where the sulphonated compounds of the wetting out type are of value. In the old days, we used soap and alkali, but in the presence of hard water, the troublesome lime and magnesia insoluble soaps were formed; this led to the use of the sulphonated compounds which form the soluble lime and magnesia soaps. The replacing of some of the alkali and soap by the sulphonated compounds has also helped by leaving the cotton in a softer condition, it being well known that alkalis leave a harsh condition.

In the bleaching processes, the sulphonated compounds have been made to help stabilize the bleaching solutions. In mercerizing, special type of compounds were needed as the ordinary sulphonated castor oil did not seem to give the required penetration. Here again, the finished goods after being treated with the strong alkali mercerizing solutions would be harsh unless treated in the last bath with some softening compounds which are found among the sulphonated compounds.

In sizing yarn, the starch compounds give too harsh a finish which interferes with weaving unless the starch compound contains something to make the sized yarn softer and more pliable. Here again, the sulphonated compounds have been found very useful, as they act as lubricating agents.

In the dyeing of cotton whether in the raw stock; yarn in the skein, warp, package or beam; and piece goods in jig, padder, continuous or other type of machine; we find much use for the sulphonated compounds in wetting out the fibre, dispersing the dye and giving uniform or level dyeing. By the use of small quantities of sulphonated compounds, all classes of dyes used on cotton such as directs, sulphurs, vats, napthols, etc., give a deeper shade which means a saving in money by using less dye.

In printing, the pastes are made smoother and more effective by use of the sulphonated compounds. A lumpy paste would be detrimental in the printing process.

In finishing, we find that a certain hand or feel is demanded by the buyer. This hand or feel can be obtained by the proper application in the right machines of compounds which in most cases contain some sulphonated product.

Wool

Wool in addition to the carbon, hydrogen and oxygen also contains nitrogen and sulphur which makes a chemical compound that differs from cotton, and naturally reacts differently with chemicals to some extent than cotton. But instead of having a waxy substance to protect the fibre from moisture, wool contains a large amount of grease, as well as other impurities. These impurities may amount to seventy-five per cent of the total weight. It is easy to see that a good detergent is needed here, and the sulphonated compounds have replaced in many cases the old formula of soap and ash. Especially is this true where hard water must be used.

After the impurities are removed, it is necessary to add some substance to assist in the spinning process. Here other sulphonated compounds are used as a base to form emulsions which are applied to the wool oftentimes in the form of a spray.

The remarks on bleaching, dyeing and finishing of cotton can be applied to wool with the addition of the following precaution. No substance should be used on wool of such a strength that the alkali contents will attack the fibre. Cotton is not harmed by alkalis but wool is very susceptible to their action. The sulphonated compounds of today have a controlled pH value which will not harm wool.

Silk

Here is a fibre which belongs to the animal class as does wool, it being the product of the silk worm. However, it does not contain sulphur like wool but does contain nitrogen which makes it chemically different from cotton. In fact, it acts like wool in dyeing in almost all cases.

The impurities of silk are not such as are found on cotton nor on wool. The principal impurity is the silk gum or sericin which is not water resistant like the wax on cotton nor the grease on wool. This sericin makes the silk fibre very harsh and somewhat brittle, so before it can be properly handled, it is usually soaked with some soaking compound. Neatsfoot oil and soap have had much use in the past, but lately, sulphonated compounds especially prepared for the purpose have come into use. After the soaking the silk can be wound into skeins, etc.

For some purposes, degumming takes place in the skein, in others the degumming is done on the finished hosiery or the piece goods. Here care must be taken that the pH does not become too high as alkali destroys silk even as it does wool, so the sulphonated compounds with a pH which can be controlled are much used.

In dyeing, we find that the facts applying to wool are also applicable to silk, that is that the sulphonated compounds are used for dispersing, penetrating and levelling properties.

In finishing of silk there are any number of special finishes required and no one compound can be expected to give the results desired, so there are numerous sulphonated compounds each having some particular object in the finishing such as dulling the lustre, reducing harsh feel, brightening, French finish, etc. The compounds are also used in some of the processes of tin weighting which is applied by use of tin or lead salts to the silk.

Rayon

This newest of fibres is treated in various processes with the sulphonated compounds. In fact, sulphonated compounds are used in some cases as a base to carry the mineral oil used in the manufacture of the rayon. This mineral oil acts as a lubricant, but by itself, it is not saponifiable nor emulsifiable. By using the sulphonated base, it becomes emulsifiable and therefore can be removed in the scouring.

The new detergent type of sulphonated compounds find use in the scouring of this fibre and do not have the harsh action of such alkali as caustic soda.

In the dyeing of the artificial fibres, with the exception of the acetate type, the compounds have the same great value as when dyeing cotton. For acetate fibres, a special type of sulphonated product has been found very useful in dispersing the insoluble type of dye for these fibres.

Oftentimes, rayon hosiery or piece goods are given special finishes whereby a dull lustre is obtained, or spot proofing, crepe effect, etc.

Here are a few advantages claimed for these compounds by various writers: K. Winokti[1] says: "Suphonated oils are claimed to have the characteristic property of preventing the precipitation of insoluble lime-soaps, or of keeping them in fine dispersion when soap is used with hard water."

A. J. Kelly[2] states: "Possibly the greatest quantity of Turkey Red Oil is used directly; as a wetting, levelling, softening or finishing agent. Its advantages are ease in handling, easy and immediate solubility, resistance to hard water and desirable finish imparted to textiles. Sulphonated oils are unaffected by and will work well in conjunction with alkalies, salts and other chemicals ordinarily added to the processing baths."

Dr. H. H. Mosher[3] said: "Uses and advantages of the glyceryl sulphates are as follows: softening and lubricating the various fibres (oleo for silk and rayon, stearo for cotton and rayon, and palmito for wool); used in dyeing, finishing, kier-boiling and as a base for emulsions. Advantages are stability with organic acids or salts, hard water and various chemicals; do not develop any odor; penetration good."

Advantages of the napthalene sulphonic compounds are the rapid and thorough wetting out properties. Used where time is valuable as it gets the scouring, bleaching or dyeing solutions into almost immediate action with the fibres.

R. Von Oesen[4] said: "Mapro products act as dispersing and penetrating agents, dissolve lime soaps, give wool a fluffy feel or hand, and are also used as softening agents in the finishing processes. These are sulphonated esters and have been found valuable especially in imparting certain hand or feel to the fabric or fibres."

R. A. Duncan[5] in writing of the sulfated alcohols says: "Some of the more striking characteristics are as follows: At suitable temperatures they are not affected by the hardness of the water. They are good sudsing and wetting agents in acid solutions. While they are slowly decomposed by acids, the rate is sufficiently slow that this change causes little or no trouble for ordinary uses. Aqueous solutions are stable in alkalies and retain their soaplike properties."

An anonymous article in the Textile World says: "What makes the sulphonated fatty alcohols of particular importance to the textile industry is the fact that they differ markedly from the soaps in that as a class, they do not hydrolize, are practically neutral in solution, having a pH value of approximately 7; are stable to acids, alkalies, hard water, concentrated solutions of common salt, etc."

In one of their booklets on "Sulfonated Fatty Alcohol Products" the Du-Pont Co. state: "The superiority of the sulfonates of the fatty alcohols over the sulfonates of the fatty acids lies in their great stability, in addition to their excellent wetting, detergent and softening properties."

Conclusion

From the foregoing, it is right easily seen that the sulphonated compounds have a close relation to the textile industry, especially that section which deals with scouring, dyeing, mercerizing, printing and finishing of yarns and fabrics.

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REPORT OF THE SOAP ANALYSIS COMMITTEE

By M. L. SHEELY, CHAIRMAN

SOAP SECTION

A Report Read Before the 8th Fall Meeting, A.O.C.S.

Publication of Complete Set of Methods of Analysis

At the meeting of the Soap Analysis Committee a year ago it was decided to adopt as the official methods of analysis of the society the Standard Methods of the American Chemical Society with certain exceptions. These exceptions included:

1. Alternative method for moisture in highly filled soaps.
2. Revised method for unsaponified and unsaponifiable.
3. Revised method for rosin.
4. Minor changes in some methods and correction of all reference notes.

It was further decided to republish the complete methods with the above noted changes and this was accordingly done in the May, 1934, issue of OIL AND SOAP.

Rosin Determination

During the course of the past year the committee has been engaged in a further study of the revised method for the determination of rosin in soap. The method is known as the Wolff Method, Modified (OIL AND SOAP, 11, 90, 1934), and consists in a double esterification of the fatty acids from the soap, the remaining detail being practically the same as the original Wolff method. The final result is obtained by a titration of the unesterified rosin and calculated to rosin by a factor corresponding to a molecular weight of 346.

Four samples, containing 0, 5%, 20% and 35% rosin in fatty acids were distributed among all members of the committee. The complete tabulated results are shown in Table I.

For the purpose of showing the effect of the second esterification, both first and second esterification results are shown. It is obvious from the table that the method still cannot be considered anything but approximate, although in general the results indicate fairly close agreement among the ten laboratories collaborating. The average of all results on the sample containing no rosin is 2.39%, the low and high figures being 1.40 and 3.32% respectively. From a comparison of these figures with results obtained by the committee last year using the same method but a different sample of fatty acid, it is apparent that the magnitude of the blank determinations may depend to some extent on the type of fatty acids involved. The committee is of the opinion that, as a result of this positive blank, a note to the effect that in all cases where less than 5% rosin is found the actual presence or absence of rosin should be checked by means of a qualitative test.

From a study of the results on the samples containing definite amounts of added rosin, varying from 5% to 35%, it is noteworthy that the method gives somewhat high results on samples containing up to and including 20% rosin, whereas at 35% rosin content slightly low results are the rule. The average of the 10 laboratories' results on the sample containing 5% rosin is 6.89%; on the sample containing 20% rosin, 20.51%; on the sample containing 35% rosin, 34.01%. At first thought, it would appear that a practical solution of the problem would be the application of a decreasing factor as the percentage of rosin increases. When such a sliding correction is applied to the present results, the percentages check fairly close with the actual percents of rosin present. However, when similar corrections are applied to last year's results the agreement would not be considered good. Consequently, the committee does not feel that it has sufficient data available to establish a table of corrections which will universally apply to all fatty acid-rosin mixtures.

In this connection it should be noted that the molecular weight of rosins will vary widely and as a consequence the titration factor used will influence results correspondingly. The rosin used in these samples was H grade having an acid number of 164, corresponding to a molecular weight of 342.1 or a N/2 factor of 0.171. However, the factor 0.173 was used in all the tabulated figures since this factor is considered to be a good average of the common rosins on the market. A meeting of the committee was held October 10, 1934, and data of the A. S. T. M. Committee D-17 on the constants of rosin were presented as follows:

	Gum Rosin		Wood Rosin	
		(Aver.)		(Aver.)
Acid number	158-172	165.0	150-158	154
Molecular weight	355.1-326.2	340.0	374.0-355.1	364.3
N/2 factor	0.1776-0.1631	0.1700	0.1870-0.1776	0.1822

This would indicate that the N/2 factor may vary from 0.163 to 0.187 or approximately a 14% variation. Consequently, it would seem inadvisable to strive for greater accuracy than this in any method involving the molecular weight of rosin.

Results by Mr. Long using methyl alcohol instead of ethyl alcohol were also submitted as follows:

% Rosin	1st Est.	2nd Est.
0	3.11	2.25
5	5.88	4.67
20	19.72	18.51
35	32.70	30.62

These results are not as satisfactory as those reported by the official method, although it should be noted that German practice specifies methyl alcohol as the esterifying medium.

Several members of the committee were of the opinion that the method in its present form is not detailed enough to follow closely and inasmuch as this may account in part for the variations noted, a recommendation to revise the procedure is recorded as a part of this report. The revised detailed method is as follows:

Summarizing, the committee wishes to make the following recommendations:

1. *Rosin Method.* This method is further revised to describe in more complete detail the actual manipulations of the method. No major changes of the procedure have been made since it is felt that the basic method is better than any heretofore published. The revised detailed method is published as a part of this report and is recommended for adoption as a tentative method.

2. *Factor to Be Used in Converting Silica* (SiO_2) *to Sodium Silicate.*

The factor used in the present methods is 1.26 corresponding to a ratio of Na_2O to SiO_2 of approximately 1:3.85. It was the recommendation of the committee that this factor be changed to 1.308 which, incidentally corresponds to the ratio of Na_2O to SiO_2 in N brand sodium silicate, namely 1:3.25. While it is recognized that