the fortunate faculty of increasing our enjoyment of food. In some cases they carry necessary vitamins, and always supply energy in a concentrated form, thus leaving a place for other interesting and important foods.

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A SIMPLE TEST TO DETECT CHLOROPHYLL IN TALLOW

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Presented Before the 8th Annual Fall Meeting—A.O.C.S.

This paper is directly concerned with the identification of green tallows. Let us consider first what we mean by a green tallow, which term we will use broadly to include all animal fat. The best definition from a soap maker's viewpoint is that a green tallow is a tallow which, when saponified in the normal manner, will produce a finished soap green in color. The raw fat may be noticeably green in color or it may carry sufficient red and yellow coloring matter to completely or partially mask the green so that the color of the fat does not appear to be green. In the kettle often sufficient of the red and yellow coloring is destroyed, changed or removed while very little of the green is lost, so that the resulting soap is green.

For soap making, the objection to the use of green tallows is that soaps made from such tallows appear definitely dull and muddy. This is true even when the green fats are mixed with non-green fats to an extent that the final soap is not definitely green.

The detergent properties of the soap containing green tallow are very little, if any, different than those of the soap made from non-green tallow. The difference is only one of appearance. The appearance of soap, even laundry soap, is very important in the eyes of a critical consuming public and a producing organization zealous to please those consumers.

There is little question but that the green color is mainly due to chlorophyll—probably introduced by contact with offal in rendering. Very little, if any, chlorophyll is normally deposited in the fatty tissues of a plant eating animal. Carotin, the orange-yellow coloring matter of leafy material, and of certain fruits and roots, such as carrots, is to some extent deposited into the fatty tissues.

Additional support to our belief that the manner of rendering and the contact with offal during rendering are responsible for green tallows are the facts that tallow from butchers' scrap is not usually green, while the Government "New Deal" pig grease from small pigs, where the whole carcass was rendered, was extremely green. The latter was equally, if not more, intensely green than the so-called "olive oil foots" or "green olive oil," which is made by solvent extraction of the olive pomace after direct pressing. Edible tallows and the lighter colored grades of inedible tallow are not usually green.

Chlorophyll is fat soluble. If fats are brought in contact with material carrying chlorophyll under suitable conditions, some of the chlorophyll will be extracted by the fat. Once the chlorophyll is in the fat, it is not easily removed. The fat may be saponified with caustic soda and pass through the various steps of soap boiling with little, if any, removal of chlorophyll.

The chlorophyll may be removed from the fat by bleaching, but this involves additional handling and expense. It is obvious that if we have two tallows of the same apparent color and otherwise equal, one containing chlorophyll and the other not, that the first is worth less than the second by the cost of the bleaching required to remove the chlorophyll.

The surest test to determine if a tallow will produce green soap is to saponify it alone and note the color of the soap it produces. This involves the killing or saponification change, a strong change, a salt wash and a pitch or settle. The grained soap of the kill and the nigre are in such physical states that usually the green color of a very green tallow is not obvious. The neat soap, especially when solid, very readily indicates variations in greenness. To properly carry out such a soap making test on a small scale requires about two days before the answer is available. Such a slow, cumbersome procedure is hardly applicable to receipt samples of shipments.

It is well known that commercial chlorophylls invariably contain copper. Pure chlorophylls are magnesium compounds equivalent to about 4.5% of magnesium oxide. The magnesium form very easily changes to the corresponding stable copper chlorophyll* so that normally the copper is introduced by processing the chlorophyll extracts in copper equipment. Some manufacturers go a step farther and add copper salts to secure a high content of the copper chlorophyll, since the latter is more intensely green than the magnesium chlorophyll and has more tinctorial power per pound. The intense green of the copper chlorophyll prompted the addition of copper salts to canned peas and other vegetables in the pre-Wiley days.

With the reactions of chlorophyll and copper in mind, we made experiments with a group of tallows of varying green content as known from the color of the neat soaps from them. Using each of these tallows, two series of attempts to change the chlorophyll in them to the copper compound were made. Each tallow was melted and two 2 oz. bottles filled about ⅔ full. To one bottle of each tallow sufficient aqueous solution of copper acetate to give 5-6 p.p.m. of copper was added and thoroughly mixed with the fat. Into the bottles of the second set a coil of clean copper wire was placed. The bottles were then kept at 60° C. for 14 hours.

Those tallows which had produced green neat soaps increased in intensity of greenness in the presence of metallic copper. Those in contact with the copper acetate solution did not give as pronounced results as the metallic copper. Further work was discontinued with the copper acetate solution since copper wire reacted quickly and was easy to apply. Further samples were given the copper treatment as well as made into neat soaps. The results further correlated the copper treated fat color with that of the soap.

Various periods and temperatures of heating were tried. It was found that the maximum intensity of green was reached in 6 hours at 60° C. or in one hour at 110°-115° C. in nearly every case.

At 100° C. about 75 minutes is satisfactory. Under these conditions the color of a non-green fat is not markedly changed.

The test as we usually carry it out is to fill two 2 oz. bottles about ⅔ full of the melted fat. Into one bottle of fat is placed a coil of clean copper wire or a strip of clean copper sheet. This bottle is then placed in an air oven and held at 110°-115° C. for one hour. The first sample is melted and both are chilled quickly in the refrigerator. When crystallization is complete, the fats are examined. The extent to which the solidified tallow has increased in green will indicate the probable color of the soap from it. The test

*The copper compound should properly be called copper pheophytins. The pheophytins are chlorophylls in which the magnesium is replaced by hydrogen. They form a salt with the metal which is very similar to chlorophyll in which the magnesium is replaced by copper. Schertz "Industrial & Engineering Chemistry," Vol. 19 (1927), p. 1152, and "Investigations on Chlorophyll" by Willstätter and Stolz, translated by Schertz and Merz, p. 236.

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.

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THE RELATION OF SULPHONATED COMPOUNDS TO THE TEXTILE INDUSTRY

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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,