

unsaturated fatty acids, as well as their esters, absorb halogens to form mainly addition products. This constant, then, may indicate to what group of unsaturated acids the resin-acids belong. Compared with iodine values of other resins, it checks with that of Elemi resin<sup>2</sup> of the *Bursera* species, they being 85.15 and 85.1, respectively.

The acid number (expressed in terms of milligrammes of potassium hydroxide required to neutralize one gramme of resin) was obtained by boiling a definite weight of resin for five minutes under a reflux with 90 percent alcohol and titrating the liquid when cold with  $\frac{N}{10}$  alcoholic potash V. S., phenolphthalein used as indicator. This constant expresses the amount of free acids present.

The ester number was obtained by subtracting the acid number for the resin from the saponification number and expresses the number of milligrammes of potassium hydroxide that would be required to combine with only the esters present in the resin.

The foregoing methods with their results afford indications of the nature of resinous substances in question, but their use in the positive identification of the various individual commercial resins is a matter of considerable difficulty even when only one resin is present, and in case of an admixture is often impossible. These constants vary and may even be entirely destroyed by aging, heating, etc. J. Lewkowitsch<sup>3</sup> has shown that the constants for various resins are absolutely destroyed by heating to 300° C. The saponification numbers, iodine values and acid numbers for the resins under examination checked after being heated to a temperature not exceeding 110° C. for two days. However, the constants for resins, including those obtained from *Datura metelloides*, may be recorded, but it is evident that any definite conclusions as to the value or purity of the resins should be drawn with the greatest care.

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## A WOOL FAT (LANOLIN) SUBSTITUTE AND THE PREPARATION OF CETYLIC ALCOHOL.\*

BY SOL. AXELRAD.

The question of substitutes for various materials has been one of prime importance during these war times, especially those substances and chemicals used in medicine and pharmacy. A year and a half ago the supply of wool fat was very limited and the price asked was four times more than that under normal conditions. A substitute called "Eucerin" imported from Germany was also scarce and the agency for this product had only four ounces left. It was claimed that "Eucerin" was made from the washings obtained in the manufacture of wool fat. The uses of lanolin are many, especially in pharmacy; as a vehicle for ointments, in the

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<sup>2</sup> Schmidt and Urban, *J. Soc. Chem. Ind.*, 8, 308, 1889.

<sup>3</sup> *Analyst*, 26, 38, 1901.

\* Contributed by the author to the *JOURNAL A. PH. A.*, October 18, 1917.

preparation of bougies, suppositories, cold creams and plasters of various kinds, etc.

This investigation on a wool fat substitute was undertaken with the idea of making a fatty composition, which would have all of the desirable properties of lanolin, such as body, tenacity, power of absorbing water readily, taking up solutions of various chemicals used in pharmacy, dry powders, etc., etc.

Liebreich claimed that the absorbing power of wool fat was due to the cholesterol ethers it contained. Lifschuetz<sup>1</sup> isolated the cholesterol ethers of Liebreich and proved that they had very little power of absorbing water. He concluded from his experiments that the absorbing power of wool fat was due to the fatty alcohols of iso- and oxysterols. He separated from the alkaline washings of partially saponified wool fat two saturated alcohols and one unsaturated alcohol. His experiments further proved that the more purified lanolin was, the lower was its power to absorb water, owing to the fact that during its purification the iso- and oxysterols were partly removed.

Unna,<sup>2</sup> in his paper, "Ointment Bases," states that "Eucerin" is a mixture of alcohols of the iso- and oxysterol group with petrolatum. He does not, however, give a commercial method for the preparation of these alcohols. The absorbing power of "Eucerin" is due to these alcohols, but Roemer (see below) claims that with the employment of sterols for ointment bases, hydrocarbons, such as mineral oil, benzol, etc., are essential, for it is due to them in combination that the absorbing property is imparted. Roemer,<sup>3</sup> in his paper on "The Pharmacy of the Oxysterol Ointment Bases," confirms to a certain extent the work of Unna, but he also fails to give a method for the preparation of the alcohols.

Unna<sup>4</sup> states that "Eucerin" has been used in skin preparations in Germany, especially in pure form for ichthyosis. According to the U. S. Dispensary, 19th Edition, page 97, experiments have been carried on in reference to the absorption of wool fat by the skin. Patschkowski and Kaspar claim that the skin readily absorbs lanolin, but Ritter and Pfeiffer in a long series of experiments were unable to verify these results. Grimm<sup>5</sup> recommends in his paper "*Ueber die Verwendung von Aethyl in der Hautpflege*," cetyl alcohol for skin preparations on account of its absorption by the skin and he further states that he has found it useful in the treatment of prurigo, weeping eczema and other skin infections.

In view of the fact that Unna and Roemer have written about the sterols, which are aliphatic higher alcohols, and Grimm has given a favorable report on the use of cetyl alcohol, the writer came to the conclusion that the use of this alcohol was advantageous in a substitute for wool fat.

A review of the literature failed to show any commercial method for the preparation of cetyl alcohol. There are many references as to its preparation from spermaceti by saponification with caustic potash and shaking the aqueous soap solution with petroleum ether, this being analogous to the extraction of unsaponifiable matter. Spermaceti is essentially the cetylic ester of palmitic acid. Chevreul, in 1818, isolated the alcohol by the above method. Krafft<sup>6</sup> prepared this substance by the reduction of palmitic acid to the aldehyde and heating it with barium formate. He also made the alcohol<sup>7,8</sup> by heating the palmitic aldehyde with zinc dust and acetic acid and hydrolyzing the acetate formed.

Levene<sup>9</sup> made this alcohol by the reduction of ethyl palmitate with sodium and absolute alcohol. Schorlemmer<sup>10</sup> distilled a dry mixture of barium oxide with sebacic acid. A method given in several text-books for the preparation of cetyl alcohol was the saponification of spermaceti with an alcoholic potash, evaporating the alcohol, taking up the residue with water, adding calcium chloride solution to form calcium soap and extracting with suitable solvents. The above methods are useful for preparing small quantities of cetyl alcohol, but for commercial quantities these methods fall down for obvious reasons.

The method of Schorlemmer was found impracticable on account of sebacic acid not being a commercial substance. The extraction process causes a considerable loss of the solvent employed and formation of troublesome emulsions.

It has been found that cetyl alcohol distils at about 340–350° C. without decomposition and the writer's method is based upon the distillation of the calcium soap of spermaceti. Various experiments were performed with the following purposes in view: 1. Greatest yield of cetyl alcohol. 2. Cheapest process. 3. Most practical method.

*Experiment I.*—Spermaceti (20 Gm.) was saponified with alcoholic potash, the alcohol evaporated and the residue heated in a distilling flask to 340° C.

*Experiment II.*—Spermaceti (20 Gm.) was saponified with alcoholic potash, the alcohol evaporated and the soap dissolved in water. To the soap solution was added excess of a 10 percent calcium chloride solution. The calcium soap was separated and dried at 100° C. and finally distilled at 340° C.

*Experiment III.*—The method employed was the same as in Experiment II, except that the soap solution was saturated with sodium chloride. The soap was filtered, dried at 100° and distilled. Many minor experiments were performed by Method III, but they did not show results of such value as to warrant their description.

*Experiment IV.*—Twenty grammes of calcium oxide containing about 5 percent water were added to 15 grammes of melted spermaceti. The mixture was heated for about six hours, with occasional stirring. When cooled, the mass assumed a brown-yellow color. On distilling same, frothing occurred at 100° C., due to the escape of water. When the water had all been driven off the temperature was raised to 340° when the cetyl alcohol distilled as white fumes and on cooling formed oily drops, which became pure white upon solidification, the melting point being 49.5° C. The yield obtained was over six grammes, this being over 40 percent of the actual spermaceti taken. The theoretical yield (calculated) was about 45 percent.

This method gave a larger yield than the other three preceding methods, and, calculating the cost of the alcohol obtained on a 40 percent basis, was also cheaper in this method. The ideal temperature for the distillation of cetyl alcohol is 330°–350°, as above this temperature a yellow liquid distils, being strongly acid and having a pungent odor; its value commercially will be investigated at a later date.

A copper still, manufactured by Sargent & Co., Chicago, for the distillation of oils, etc., at high temperatures, was found to be of most service. Glass stills are apt to crack, due to the "caking" of the residue which can readily be removed from the copper still, after each distillation.

Mixtures were made having different quantities of base, cetyl alcohol, lanolin and water. The formula finally selected as being the best suitable for pharmaceutical compounding was the following: 70 parts petrolatum, 20 parts paraffin (m. p. about 60° C.), 10 parts cetyl alcohol, 5 parts lanolin (anhydrous), 100 parts water. This preparation stood in the laboratory for 17 months with absolutely no change in appearance or working qualities. The properties of this mixture are the same as wool fat, that is, taking up solutions of salts, powders, etc., etc. The advantage over wool fat is that it will not become rancid and is considerably cheaper. The reason for using 5 parts of lanolin in the mixture was to have the "unctuous" property of wool fat. This, however, is a minor physical property.

A cold cream having very desirable properties can be made by using the above formula except for the addition of 250 parts of water instead of 100. The method of mixing the various substances is of prime importance. The petrolatum, alcohol, lanolin and paraffin are melted together. The water is warmed to the same temperature as the melted fats and added slowly with constant grinding so as to get a smooth mixture.

Microphotographs of hydrous wool fat, the substitute, and cold cream have been taken and are shown below.

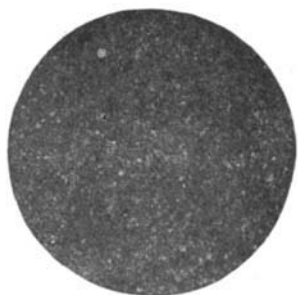


FIG. I.—HYDROUS LANOLIN.  
(Wool fat with 30 percent water.)  
Average cost per pound, 40 cents.

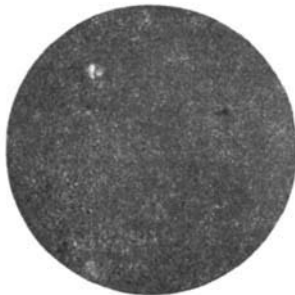


FIG. II—WOOL FAT SUBSTITUTE.  
55 to 75 percent cheaper than  
hydrous lanolin.

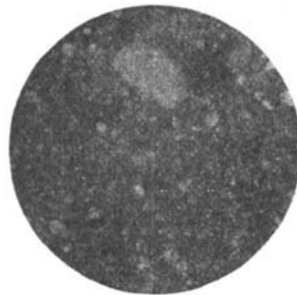


FIG. III.—COLD CREAM.  
80 to 90 percent cheaper than  
hydrous lanolin.

The writer believes that the wool fat substitute described in this paper will stand competition with wool fat and "Eucerin," both now and under normal conditions.

A further investigation is under way to determine the value of ceryl alcohol,  $C_{27}H_{55}OH$ , from Chinese wax and myricyl alcohol,  $C_{30}H_{61}OH$ , from Carnauba wax for the same purpose for which cetyl alcohol,  $C_{16}H_{33}OH$ , from spermaceti was put to, namely, in the preparation of a wool fat substitute.

In conclusion, due credit is hereby given to Mr. Sol. Bernstein, who spent considerable time in performing experiments and assisting in general to bring this paper to a successful issue.

1. *Berichte*, Vol. 29, p. 2890.
2. *JOURNAL A. PH. A.*, Vol. I, p. 673.
3. *Ibid.*, Vol. II, p. 971.
4. *Proc. Royal Society of Medicine*, London, 1911-1912, p. 220.
5. *Dermatologische Zeitschrift*, Vol. 6, p. 158.

6. *Berichte*, Vol. 13, p. 1416.
7. *Ibid.*, Vol. 16, p. 1721.
8. *Ibid.*, Vol. 17, p. 1627.
9. *J. Biol. Chem.*, Vol. 20, p. 121.
10. *Berichte*, Vol. 3, p. 616.

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"Technology of Oils and Fats," by Lewkowitzsch, p. 239.  
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## METHODS OF ANALYSIS OF ACETYSALICYLIC ACID AND ADULTERANTS.

BY HENRY L. SCHULZ.

With the collaboration of C. K. Glycart, A. W. Hanson and A. E. Stevenson.

In the spring of 1915, about ten months after the outbreak of the European war, the supply of acetylsalicylic acid was practically exhausted. The stocks still held by a few dealers were being offered at an advance of about two hundred percent above the market price of the previous year. Owing to the scarcity of synthetic drugs of foreign origin, the "drug peddlers" and "drug brokers" who had been dealing in these products were unable to supply the demand and, not wishing to lose an opportunity to profit by the advanced prices, resorted to unscrupulous methods to obtain material for their trade.

Information that acetylsalicylic acid was being adulterated reached the Department in the early part of June 1915. An investigation was begun and samples collected and analyzed. These samples, mostly tablets, showed a marked variation in composition. Some were pure acetylsalicylic acid, others contained only small amounts, and a number did not contain any. As the combinations of substances found in the spurious samples differed widely, it was concluded that several manufacturers were adulterating acetylsalicylic acid, and steps to locate them were immediately taken. After some difficulty, consignments of spurious acetylsalicylic acid were found to have originated in Cleveland, Indianapolis, Memphis, St. Louis and Chicago. For the purpose of hiding their identity and to make it more difficult to trace shipments, some of these adulterators would use fictitious shippers' names and addresses on the packages sent out by them.

Previous to 1917, before the patent on acetylsalicylic acid expired, its sale was restricted in this country, and reputable wholesale druggists refused to handle it except under the trade name "Aspirin." As stated above, most of the acetylsalicylic acid was sold by drug brokers and peddlers who frequently carried their entire supply in a trunk or suitcase and disposed of it in such quantities as the druggist or dealer might wish to buy. A number of the shipments sent to brokers and peddlers by these adulterators were located and immediately confiscated by inspectors of this Department. The investigation showed that some of these manufacturers would deliver the unlabeled, spurious mixture to manufacturing pharma-