

[54] METHOD OF PURIFYING ALKALI METAL
SOAPS OF SYNTHETIC FATTY ACIDS[75] Inventors: **Hideomi Saito**, Sagamihara; **Takashi Yamashita**; **Takuro Munezawa**, both of Yokohama; **Tetsuya Kato**, Fujisawa, all of Japan[73] Assignees: **Ajinomoto Co., Inc.**; **Japan Carboxylic Acids Co., Ltd.**, both of Tokyo, Japan; a part interest to each[22] Filed: **Apr. 13, 1973**[21] Appl. No.: **350,772**

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[56]

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ABSTRACT

Fatty acids obtained by oxidation of paraffin wax are purified by extraction of the aqueous solutions of their alkali metal salts with ethylene dichloride in the presence of enough methanol, ethanol, or propanol to prevent emulsification of the extraction mixture. Ethylene dichloride is more effective and less inflammable than the conventional low-boiling petroleum fractions employed heretofore and makes the use of methanol practical.

5 Claims, No Drawings

METHOD OF PURIFYING ALKALI METAL SOAPS OF SYNTHETIC FATTY ACIDS

This invention relates to the removal of unsaponifiable matter from fatty acids substantially insoluble in water, and particularly to a method of purifying alkali metal soaps of synthetic fatty acids from contaminating unsaponifiable matter.

The invention is not limited to synthetic fatty acids produced by any specific method, but will be described hereinafter with reference to the purification of alkali metal soaps of fatty acids produced by oxidizing paraffins having about 10 to 50 carbon atoms. (British Pat. No. 1,143,213 and Paraffins, Chemistry and Technology edited by H. M. E. Steiner (1968), Pergamon Press)

It has been common practice heretofore to convert crude synthetic fatty acids to their alkali metal soaps by treatment with aqueous alkali metal hydroxide solutions, and to subject the soap solution to superheated steam distillation or to extraction with organic solvents not miscible with water. The most widely applied method involved extraction with gasoline in the presence of enough ethanol or propanol to prevent emulsification of the two phases and promote their rapid separation into two layers after completion of the extraction. The distribution ratio of the unsaponifiable matter in the known system is not favorable so that the soap solution needs to be contacted with twice its volume or more of the gasoline in each extraction step. Gasoline is dangerous to handle because of its flammability.

It has now been found that ethylene dichloride may replace the gasoline in the conventional process, and offers advantages well beyond the obvious one of greater safety due to its relatively high flash point of 15°C.

The partition coefficient for the unsaponifiable matter in simultaneous contact with alcoholic soap solution and ethylene dichloride is much more favorable than that for gasoline so that a small amount of the chlorinated solvent is as effective as a much larger amount of gasoline. Moreover, methanol may be employed for preventing emulsification in the presence of ethylene dichloride, but the use of the inexpensive methanol in the conventional method is not practical on an industrial scale.

The nature of the alkali metal in the soap solution is not relevant in the known method nor in that of the instant invention. The potassium and sodium salts may be used interchangeably, but economical considerations normally favor the sodium salts.

A portion of the unsaponifiable matter, mainly consisting of unreacted paraffin, may be removed prior to ethylene dichloride extraction as it is often removed prior to gasoline extraction, and the amount of alcohol that needs to be present during extraction depends largely on the amounts of water and unsaponifiable matter still present in the refined soap solution and may vary between 5 and 50 percent of the weight of the soap solution. Good results are normally achieved with 10 - 35 percent methanol or 10 - 27 percent ethanol or propanol. Too much alcohol may result in the formation of a homogeneous solution rather than the desired two distinct layers.

The temperature at which the extraction is carried out is not critical, the temperature limits being set inherently by the freezing point of the aqueous phase and the boiling point of ethylene dichloride (83.7°C). Be-

cause the extraction rate is accelerated by higher temperature, the preferred range of operating temperatures is between 40° and 75°C. The extraction may be carried out in a system under the pressure of the ambient atmosphere or at elevated pressure, such as 5 atmospheres.

When the method of the invention is carried out batchwise, the extraction mixture is permitted to separate into layers by gravity. The lower solvent layer contains practically the entire unsaponifiable matter, and the aqueous layer contains the soap, the alcohol, and a small amount of the chlorinated solvent. In continuous operation, the heavy solvent is fed to the top of an extraction column and the contaminated, alcoholbearing soap solution to the bottom. The column should have at least two plates or their equivalents, and four to 10 plates or their equivalents may be beneficial.

The solvent phase is separated from the aqueous phase and fractionated to recover the ethylene dichloride and the unsaponifiable matter, and the aqueous phase may be exposed to elevated temperature or treated under reduced pressure for volatilizing the alcohol and the small amount of ethylene dichloride which is soluble in water. The purified soap solution may be employed as such or it may be acidified to separate purified fatty acids, as is conventional in itself.

The amount of ethylene dichloride employed for extraction varies with the degree of contamination of the soap with unsaponifiable matter and the degree of purification that it is desired to achieve. Under otherwise equal conditions, the volume of ethylene dichloride that needs to be handled is a fraction of the gasoline volume needed for achieving an analogous result. The weight ratio of the ethylene dichloride to the alcoholbearing, contaminated, aqueous soap solution should be between 0.1:1 and 5:1 under most normal conditions, and favorable results are usually achieved within the narrower range of 0.2:1 and 2:1.

The following Examples are further illustrative of the invention.

EXAMPLE 1

Paraffin wax (m.p. 125°F) was oxidized in a conventional manner to produce a crude mixture of fatty acids, and the mixture was saponified with aqueous sodium hydroxide. The saponification mixture was held in a nitrogen atmosphere at 20 atmospheres and 200°C for 2 hours. Unsaponifiable matter, mainly consisting of unreacted paraffin, separated from the aqueous phase and was removed. The aqueous mixture consisted of 39.5% soap, 11.2% unsaponifiable matter, and 49.3% water, all percentage values in this application being by weight unless specifically stated otherwise.

Two 100 g batches of the aqueous liquid were each mixed with 25 ml methanol, and two other batches with 20 ml ethanol. One methanol-bearing and one ethanol-bearing batch were each extracted twice at 65°C with 100 ml of a gasoline fraction boiling between 80° and 110°C. The two other batches were extracted under the same conditions with ethylene dichloride.

The four aqueous liquors so obtained were separated from the organic solvent phases and heated to remove the alcohol and the extracting agent. The remainder was acidified with sulfuric acid. The fatty acids were recovered and analyzed for residual unsaponifiable matter. It was found that the gasoline had removed 34 percent of the original unsaponifiable matter in the

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presence of methanol and 41 percent in the presence of ethanol. The corresponding values for ethylene dichloride were 85 and 88 percent.

EXAMPLE 2

Another batch of crude fatty acids obtained by oxidation of paraffin wax in the same manner as in Example 1 was refined by continuous heating for 10 minutes at 260°C in the presence of silica-alumina catalyst, as is known in itself. The refined fatty acid mixture was saponified with aqueous sodium hydroxide solution, and the saponification mixture was treated similarly as in Example 1 so as to remove unsaponifiable matter mainly consisting of unreacted paraffin. The resulting soap solution consisted of 37.8% soap, 10.2% unsaponifiable matter, and 52.0% water.

One 100 g batch of the soap solution was mixed with 25 ml methanol, and another batch with 20 ml ethanol. Both were extracted twice with 100 ml ethylene dichloride, the aqueous liquids were heated for removal of alcohol and solvent, and the fatty acids recovered from the purified aqueous soap solutions were analyzed for residual unsaponifiable matter. 83 Percent of the unsaponifiable matter was removed from the methanol-bearing solution and 87 percent from the ethanol-bearing solution.

EXAMPLE 3

A crude soap solution was prepared and subjected to a preliminary refining treatment in the same manner as in Example 1. The refined solution was mixed with methanol in a volume ratio of 4:1, and the mixture was fed at a rate of 1.25 liter per hour to the bottom of a jacketed column 1000 mm high and 50 mm in diameter which was packed with Raschig rings 6 mm in diameter. Ethylene dichloride was fed simultaneously to the top of the tower at a rate of 500 ml per hour. The contents of the tower were held at 65°C by means of the heating jacket.

The soap solution overflowing from the top of the tower was collected in a tank, and the contents of the

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tank were withdrawn from time to time, heated to volatilize the methanol and ethylene dichloride present, and acidified with sulfuric acid. The fatty acid mixture obtained by decomposition of the soap was washed with water and analyzed. It contained only 2.4% unsaponifiable matter.

What is claimed is:

1. A method of purifying an alkali metal soap contaminated with unsaponifiable matter and prepared by oxidizing paraffin to an oxidation product essentially consisting of fatty acids substantially insoluble in water and containing said unsaponifiable matter, and holding said oxidation product under saponifying conditions, said method comprising:

- a. preparing an aqueous solution of said contaminated soap and of a lower alkanol, the amount of said alkanol being 5 to 50 percent of the weight of said solution;
- b. extracting said solution with ethylene dichloride until said saponifiable matter is substantially completely extracted from said solution and dissolved in said ethylene dichloride,
 1. the amount of said lower alkanol being sufficient to prevent the formation of an emulsion from said aqueous solution and said ethylene dichloride; and
- c. separating the extracted aqueous solution from the ethylene dichloride having said unsaponifiable matter dissolved therein.

2. A method as set forth in claim 1, wherein said paraffin has 10 to 50 carbon atoms.

3. A method as set forth in claim 1, wherein said lower alkanol is methanol.

4. A method as set forth in claim 2, wherein said amount of said methanol is between 10 and 35 percent of said weight.

5. A method as set forth in claim 1, wherein an aqueous solution is first prepared from said contaminated soap without said alkanol, and said alkanol is added to said first-prepared solution prior to said extracting.

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