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SOAP MANUFACTURE

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This invention relates to the manufacture of soap and is more especially concerned with the preparation of oil soluble metal soaps of wax acids.

The crude wax acids obtained by blowing molten paraffin, petrolatum or similar waxy materials with air under controlled conditions is in the nature of a mixture of organic acids, alcohols, aldehydes, ketones, and possibly lactones and lactides, of various kinds and carbon content, together with small amounts of unreacted starting material. While the whole mixture may occasionally be used without further refinement, it is generally desirable to separate it into one or more fractions having special utility in themselves or as the starting materials for the preparation of other products.

The conventional method of stripping the hydroxy acids from mixtures of this kind preparatory, for example, to the formation of oil soluble soaps of the residual carboxylic acid fraction, involves the treatment of the wax acids with as much as ten volumes of naphtha, giving rise to the separation out of a small amount of insoluble hydroxy acid material, and of then precipitating naphtha-soluble hydroxy acids by treating the solution with ortho phosphoric acid. The hydroxy-acid-free oxidation products recovered from the naphtha solution following this treatment are essentially carboxylic acids together with alcohols, aldehydes, ketones, etc. which may be converted to salts by reaction with a selected metal oxide or hydroxide.

The foregoing process is objectionable from the standpoint of the long time which is required to effect substantially complete precipitation of the hydroxy acids from the naphtha solution. Thus the solution must be treated repeatedly with small volumes of ortho phosphoric acid, and be left to stand for a period of about two hours between each acid dump for the settling out of the very fine precipitate which is formed. In actual practice, for example, the treatment is usually repeated four or five times in order to effect an adequate separation of the precipitatable matter. A further objection to this process arises from the difficulty and expense which is attendant upon the recovery of the phosphoric acid—a step which must be taken, however, if the process is to be carried out on a commercial scale.

Further problems arise in the preparation of soaps of the wax acids which are recovered in the foregoing or in any other way. This is particularly so when these, or in fact fatty acids of

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any kind, are to be converted to soaps by the conventional double decomposition process involving saponification with sodium hydroxide, for example, and the subsequent reaction of the sodium soap which is thus formed with the compound of the selected metal to yield a final desired product. The difficulties which are encountered in the washing of the water insoluble final soap to remove all traces of sodium salts, etc., and the losses which are occasioned by the formation of emulsions in the course of this tedious washing operation, are so familiar to those skilled in the art as hardly to require detailing here.

The principal object of the invention is to provide a double decomposition method for the preparation of a soap of a selected metal and an organic acid derived from wax, natural fats, oils or other sources, which is easier to carry out, less consuming of expensive chemicals, and results in a smaller loss of reaction products than the methods which are conventionally employed in making products of this kind.

It is a further object of the invention to provide a method for forming an oil soluble soap of a selected fraction of crude wax acids which avoids the troubles incident to the refining of crude wax acids by phosphoric acid precipitation, as well as those which arise in the conversion of the wax acids to the final metal salt by double decomposition as conventionally practiced in the prior art.

Other objects, and various features will be brought out in the following description of my new process as illustrated by several specific examples.

In the application of the invention to the preparation of an oil soluble wax acids soap, a crude mixture of oxidation products obtained by the controlled air-blowing of paraffin or other waxy material, is first refined to eliminate substantially all of the hydroxy acid constituents, leaving a fraction consisting essentially of carboxylic acids and esters for conversion into oil-soluble soap of the desired kind. In preparing such a carboxylic acids fraction by my method, a suitable batch of crude wax acid is first cut with at least four volumes of naphtha to give a solution from which the hydroxy acid fraction may be precipitated by contact with concentrated sulphuric acid ranging from about 75 per cent strength up to fuming grade. Thus, excellent results may be obtained by adding 66° Bé. sulphuric acid to such a solution in an amount representing from 4 to 10 per cent by weight of the dissolved crude wax acids, and by stirring this mixture for a period of from 5 to

20 minutes to assure adequate contact between the inorganic acid and the dissolved wax acids.

Upon completion of this treatment, the mixture should be permitted to stand for a period of time sufficient to permit it to settle into two well-defined layers. The lower of these layers consists essentially of hydroxy acids accompanied by some alcohols, aldehydes and ketones, together with substantially all of the sulphuric acid which was added as a precipitant. This layer may therefore be drawn off into 3–4 volumes of water to dilute the sulphuric acid to the point where it will separate out and leave a mixture of the hydroxy acids, and possibly some naphtha, for further refinement and treatment in any suitable way.

The clear naphtha solution which remains after the drawing off of the sulphuric acid-hydroxy acids contains the balance of the crude oxidation products in the form of hydroxy-free acids and esters as major ingredients, together with a small percentage of alcohols, aldehydes, ketones and possibly lactones and lactides, this mixture, for want of a better term, being referred to as the "carboxylic acids" fraction. It will be evident that the foregoing steps deal only with initial separation of the crude oxidation products, and the preparation of a fraction which is suitable for conversion into metal soaps of a desired character. In accordance with my invention, this conversion is effected by double decomposition in which the naphtha solution is first treated with ammonia, in dry or aqueous form, in such quantity as to convert the organic acids and ester constituents into ammonium soaps, and in which those soaps are then reacted with a compound of a selected metal to displace the ammonia and yield the desired metal soap as a final product.

It is of note that the foregoing reaction is carried out at a temperature which is high enough to drive off all of the ammonia, along with such water as may be present, the ammonia being recovered for reuse. Upon its completion, the naphtha may readily be flashed off and recovered, thus leaving a mixture of metal soaps of the carboxylic acids fraction of the original crude wax oxidation products, together with unreacted alcohols, aldehydes, ketones and oxidation products. The product which is so recovered will obviously be free of ammonia, and accordingly requires no washing or other supplementary treatment to prepare it for immediate use.

The complete process of extracting a carboxylic acids fraction of crude oxidation products and conversion of that fraction to metal soap in the foregoing manner is obviously more expeditious, less troublesome, and very much more economical than prior art methods of accomplishing the same results. It is of particular note, however, that the soap making phase of the invention is not limited to use in the treating of a particular wax acids fraction. On the contrary, it appears to be one of general application to the preparation of soaps from natural fats and oils, and is particularly useful in the preparation of heavy metal soaps of fatty acids from any source.

Example I

The starting product for this example was prepared by blowing molten scale wax (M. P. 122–126° F.) with air at substantially atmospheric pressure, and at a temperature of from 300–315° F. for a period of about 30 hours. In the course of this reaction substantially all of the hydrocarbons were oxidized to a greater or lesser extent, giving a final product which consisted essentially of organic acids, aldehydes, esters, ketones, lactones, and lactides, together with a small percentage of unreacted wax. This particular mixture proved to have a neutralization number of about 67 with a saponification number of approximately 130.

In carrying out my process, a 100 gram sample of the foregoing crude wax acids was treated with 400 cc. of Pennsylvania straight run naphtha having a boiling range of 150–250° F., i. e., in a ratio of about one volume of oxidation products to four volumes of naphtha. From a practical point of view, this seems to represent about the lowest ratio of wax acids to solvent which can be successfully employed. The crude wax acids may, however, be cut to a very much greater extent than I have indicated, and if the dilution is carried far enough, say to a ratio of about 1:10, some hydroxy acids may be precipitated out in this step. The amount of hydroxy material which can be separated out in this way is usually so small as hardly to warrant the added cost of handling the larger volume of solution throughout the process, and particularly of flashing off and recovering the extra naphtha in its final stage. In general, therefore, I prefer to use the minimum amount of naphtha which will yield a solution from which the hydroxy acid fraction may be precipitated by contact with concentrated sulphuric acid, and thus to gain the advantage of the smaller volume of liquid to be handled in the process.

In order to precipitate the hydroxy acid materials from the foregoing solution, I added 4 cc. of concentrated sulphuric acid (66° Bé.) representing approximately seven per cent of the weight of the original wax acids sample. It is essential to the successful carrying out of this step that good contact be established between the sulphuric acid and the entire naphtha solution, a result which was accomplished by a thorough stirring of the mixture for a period of about twenty minutes.

At the conclusion of the acid treatment, the solution was allowed to stand for a period of time sufficient to permit the settling out of the precipitated oxidation products along with the added inorganic acid. In the instant case, about two hours of standing sufficed to establish two clearly defined layers of which the lower was drawn off for the recovery of both the sulphuric acid and oxidation product constituents. Such a recovery was readily effected by diluting the precipitate with about three volumes of water and by heating the resulting mixture to a temperature of from 175°–200° F. with vigorous stirring preparatory to settling out the dilute sulphuric acid. Upon the drawing off of the latter, the remaining greenish-amber colored oil layer was washed again with water to eliminate any traces of sulphuric acid, thus giving a product representing about 23 per cent (by weight) of the original wax acids, and consisting primarily of hydroxy acids and secondarily of alcohols, esters, ketones and other oxidation products in such a condition that they may readily be refined or further treated in any suitable manner.

It will be evident therefore that the foregoing steps deal only with the preparation of what I call "carboxylic acids fraction" of the crude wax acids, for conversion into metal salts of a desired kind. These hydroxy-acid free oxidation products, as retained in the clear naphtha solution following the drawing off of the precipitate in the foregoing manner, may be further refined in

any suitable way to increase the concentration of the organic acids and esters, and to eliminate at least some of the alcohols and other non-saponifiable matter. In preparing oil-soluble soaps for use as lubricating oil addition agent, however, I find that such further refinement only adds to the cost of the process without improving the end product and that, in fact, the presence of the solvent alcohols, ketones, etc., in the final product is desirable. The whole naphtha solution was accordingly transferred to a flask fitted with a reflux condenser where I added approximately 50 cc. of concentrated ammonium hydroxide, this quantity representing that theoretically required for saponification of the organic acids and esters, plus about 20 per cent excess. The resulting solution was heated to assist in the saponification, which started when the temperature had reached about 150° F., and was completed at a temperature of from 175–185° F. after a reaction period of about two hours.

In order to convert the ammonium salts of the foregoing reaction to magnesium soaps for use as oil addition agents, I added a water slurry containing ten grams of magnesium oxide to the naphtha-soap solution, and continued refluxing for a period of about three hours at a final temperature of around 220° F. The ammonia which was displaced in this reaction was driven off with water, and was recovered as ammonium hydroxide for reuse in the process. At the end of this replacement reaction, the naptha solution was permitted to stand for the settling out of excess magnesium oxide, the clear solution was then filtered, and the naptha flashed off and recovered, leaving a mixture of magnesium soaps along with unreacted alcohols, aldehydes, ketones and other nonsaponifiable matter.

The reaction product which was so recovered represented about 77 per cent of the weight of the original wax acids sample of which 30 per cent was magnesium soap (based upon assumed average molecular weight of 220 for the acids involved) containing about 2.02 per cent by weight of magnesium. It is of particular note that this product was uncontaminated by ammonia or its compounds, and required no water washing or other after treatment to prepare it for ultimate use.

The results of a repetition of the process upon three additional 100 gram samples taken from the batch of crude wax acids which was described briefly above, in terms of the magnesium reaction product recovered from the final naptha solution, are tabulated below:

Sample	Magnesium Reaction Product, grams	Magnesium Soap Content, (Per Cent)	Contained Magnesium, (Per Cent)
a	74	31.9	2.23
b	75	30.9	2.14
c	75	34.8	2.40

The quantity of hydroxy acid material which may be separated out in any given case, as well as the yield of final metal reaction product, will of course depend upon the nature of the wax acids under treatment, that is to say, upon the character of the hydrocarbon which has been subjected to oxidation, the length of oxidation treatment and the pressure, temperature and other process factors employed, all as is well understood in the art. This was demonstrated by a repetition of my process, in both its separatory

and soap-forming steps, upon four different samples of crude wax acids which were obtained by blowing molten paraffin with air for increasingly long periods of time. In each case a 100 gram sample of oxidation product was employed, and that sample was in each instance cut with about 400 cc. of straight run naptha of the kind previously mentioned. The characteristics of the several samples of oxidation products, the quantity of sulphuric acid added to precipitate their hydroxy-acid fractions, and the yields obtained in each case are tabulated below:

Sample No.	1	2	3	4
Neutralization No.	34.6	48.7	55.8	61.5
Saponification No.	74.6	106.0	125.1	148.6
Sulphuric acid (66° Bé.) cc.	2.0	2.5	3.0	3.0
Hydroxy-acids grams	4.0	8.0	11.0	15.0
Mg. Reaction Product do	99.0	93.0	92.0	82.0
Contained Magnesium per cent	3.33	3.33	3.5	2.29

Example II

The soap making steps of my method are fully applicable to the treating of wax acids fractions prepared in other ways than the preferred one which has just been described. By way of illustration, a sample of the crude oxidation products referred to in Example I was cut with naphtha in a ratio of about 1:10 by volume, and the hydroxy acid constituents were then precipitated out by treatment with phosphoric acid in accordance with well understood prior art practices. The carboxylic acid fraction which was separated out in this fashion represented about 69 per cent (by weight) of the crude product under treatment. A 50-gram sample of this product, dissolved in about 400 cc. of straight run naphtha (150–250°) was placed in a flask fitted with a reflux condenser along with 25 cc. of concentrated ammonium hydroxide solution, and the mixture was heated at reflux temperature for a period of about two hours, to convert the acid and ester constituents of the solution to ammonium salts. At the end of that period, a slurry of 5 grams finely ground magnesium oxide in about 15 cc. of water, was added to the flask and heating was continued for an additional two hour period at reflux temperature. During the course of the reaction of the magnesium oxide and ammonium salts, naphtha was taken off overhead so that the boiling point of the mixture gradually rose to about 210–215° F. with a consequent driving off of both ammonia and water. When it appeared that all the water had been eliminated, the mixture was cooled, allowed to settle and then clarified by filtration.

Upon the conclusion of the foregoing, the naphtha was then distilled off, leaving a mixture of magnesium soap and unreacted alcohols, aldehydes and ketones. It is of note that the 48.5 grams of product which were recovered contained approximately 2.28 per cent by weight of magnesium; and that the product was in substantially pure form ready for use as a magnesium wax acids soap.

Example III

The new soap making method has also been applied with complete success to the treatment of naturally occurring oils and fats of both animal and vegetable origin. In one case, for example, soya bean oil was treated with concentrated ammonium hydroxide to yield an ammonium soap for subsequent reaction with a metal compound. This saponification reaction does not proceed

readily at atmospheric pressures, but may easily be carried out at a pressure such as to hold the ammonia in contact with the oil. In the instant case, the natural oil and ammonium hydroxide were reacted under the autogenous pressure generated by heating these ingredients in a closed bomb at a temperature of about 212° F. The ammonia soap product thus formed, was then dissolved in naphtha, and a slurry of magnesium oxide in water was added to the solution for the purpose of displacing the ammonia and forming a magnesium soap, this reaction being carried out under reflux conditions with continuous take-off of light naphtha fractions so that the temperature rose gradually to about 215° F., with a consequent driving off of both the ammonia and water. When it appeared that all of the water had been displaced, the solution was settled and filtered and the naphtha was then distilled off, leaving magnesium soap as the principal product.

The glycerine which was formed in the saponification reaction may be removed at the completion of that step or later, as may be most expedient. In the instant case, it was extracted with water after the completion of the soap making operation, thus yielding a final soap containing 6.36 per cent by weight of magnesium. It will be evident that this metal content is somewhat in excess of its theoretical content of about 4 per cent, the difference being accounted for by the presence of a molecule of combined MgO.

The natural acid and ester constituents of a lard oil have also been converted to magnesium soap by following precisely the technique described above. Thus saponification was carried out with concentrated ammonium hydroxide under the autogenous pressure developed in the course of heating this mixture in a closed bomb at a temperature of about 212° F., and by reacting the resulting ammonium soaps, in naphtha solution, with magnesium oxide. The soap which was recovered upon the driving off of naphtha and extraction of its glycerine content, was found to contain 6.65 per cent by weight of magnesium, this again being in excess of the theoretical metal content of the finished product and apparently attributable to the presence of a molecule of combined MgO.

It is of note that both the soya bean and lard oils were reacted with ammonium hydroxide in the absence of any intervening solvents because of space limitations of the particular bomb which was available. In general, it appears that the reaction proceeds more easily and readily when the oils are first dissolved in naphtha, and the ammonium soap product is then recovered in the liquid form which may be handled most easily in the final stages of the process. We prefer therefore to cut the oils with naphtha in suitable ratio, and to treat the resulting solution with ammonium hydroxide or dry ammonia gas, and then to carry out the metal replacement step just as heretofore described.

It will be observed that the foregoing specific examples deal only with the preparation of magnesium soaps of various organic acids and esters. In other instances, and by following precisely the general method which has been described, I have reacted copper and calcium compounds with the ammonia soaps to yield final soaps of those metals, and various tests indicate that the method is fully applicable to the preparation of lead, silver, cobalt and aluminum soaps, and seemingly soaps of any selected metal. Insofar as the character of the metal compound is concerned, I prefer to use the oxides and hydroxides of the selected metal, and in appropriate cases, the carbonates and chlorides, to form ammonium reaction products which readily break down upon heating so that both the ammonia and other constituents will separate from the finished metal soap and pass off with the effluent vapor, thus avoiding the necessity of washing the finished metal soap or subjecting it to other after treatment.

It is of further note that the invention is not limited to the preparation of soaps of the specific fatty acids and esters which have been considered in the several examples. On the contrary, as those familiar with the art will recognize, fatty acids and esters may be prepared from various paraffinic and naphthenic petroleum fractions, as well as from animal and vegetable products, and are all suitable for conversion to soaps in the foregoing manner.

Having described my invention in its broadest aspects and illustrated it by way of specific examples, what I claim as new and useful is:

1. The process of making an oil soluble soap of wax acids which comprises the steps of treating a naphtha solution of substantially hydroxy-acid-free oxidized petroleum wax with ammonia in such quantity as to convert its organic acid-ester constituents to ammonium salts, reacting such salts in naphtha, solution with magnesium oxide to convert them to magnesium soaps, said reaction being carried out at a temperature such as to drive off the displaced ammonia and water, and separating the magnesium soaps from the naphtha solution.

2. The process of making a metal soap, which comprises the steps of dissolving substantially hydroxy-acid-free oxidized petroleum wax containing acidic components in naphtha, treating such solution with ammonia to form ammonium soaps of the acidic components of such material, reacting such ammonium soaps in naphtha solution with a metal compound selected from the group consisting of the oxides and hydroxides of magnesium, calcium, and copper to convert them to metal soaps, heating the resulting mixture at a temperature such as to break down and drive off ammonia compounds which are formed in the last-mentioned reaction, and recovering the metal soaps from the naphtha solution.

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