

UNITED STATES PATENT OFFICE

2,166,812

PROCESS FOR THE SEPARATION OF THE
CONSTITUENTS OF ORGANIC MIXTURES
CONTAINING BOTH RESIN ACIDS AND
FATTY ACIDS, PARTICULARLY TALL OILFrederick H. Gayer and Charles E. Fawkes, Chi-
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tion of IllinoisNo Drawing. Application October 18, 1937,
Serial No. 169,654

17 Claims. (Cl. 260-107)

This invention relates to an improved process for the separation and recovery of the major constituents of organic mixtures or oils containing both resin acids and fatty acids, and particularly to the clean, sharp and economic separation and recovery of the resin acids and the fatty acids from such mixtures or oils, and particularly from tall oil.

Tall oil is a by-product of sulphate or kraft paper manufacture, and is obtained by acidification of the black liquor soap, which is salted out and rises to the surface of the black liquor on standing. The main constituents of tall oil include fatty acids, resin acids and unsaponifiable substances. While the bulk of the unsaponifiable matter consists of hydrocarbons, it also contains a considerable proportion of high-molecular weight cyclic alcohols belonging to the group of phytosterols.

Tall oil as such has found relatively little commercial use. It is not suited for soap making on account of its dark color, its odor and its high resin acid content, nor can it be used as a substitute for rosin or other natural resins on account of its fatty acid content. On the other hand, the components of tall oil, especially the resin acids, fatty acids and phytosterol are of considerable commercial value. Therefore, a process for the sharp separation of the components of tall oil would be of great commercial value, especially in view of the vast potential supply of tall oil, resulting from the increasing importance of the sulphate process for paper making. Due to its low commercial value, tall oil is usually not even recovered in the present sulphate pulp establishments.

Numerous processes have been described relating to the separation of the components of tall oil. For example, United States Patent No. 1,986,815 proposes to refine tall oil by allowing a portion of those components possessing a higher melting point, such as resin acids and higher saturated fatty acids, to settle out on standing. It is obvious that no separation of resin and fatty acids can be effected by such a process. A well known method for the separation of resin and fatty acids of tall oil is based on distillation in vacuo, as exemplified by United States Patent No. 1,826,224. Since the fatty acids distill at a lower temperature than the resin acids, it is possible to effect a rough separation by distillation. However, the method has the limitation of all distillation methods, and even when using expensive fractionating equipment will not give a profitable yield of fatty acids free of resin

acids. Another method, proposed by United States Patent No. 1,921,566, is based on the esterification of the fatty and resin acids with a polyhydric alcohol. The separation in this case is effected by subjecting the mixture of esters to hydrolysis in such a way that only the fatty acid esters will be hydrolyzed. The resulting fatty acids are separated from the unchanged resin acid esters and the unsaponifiable matter by distillation. A simpler method is proposed by United States Patent No. 1,736,802. According to this method, only the fatty acids are esterified with ethyl alcohol. The mixture of fatty acid esters and resin acids is dissolved in a hydrocarbon solvent. From this solution the resin acids are separated by an aqueous alkali solution as water soluble soaps. The shortcomings of this method are the retention of a portion of the resin acid soaps in the hydrocarbon-ester layer, and the unavoidable formation of stubborn emulsions preventing a clear separation into layers even after adding a considerable proportion of alcohol to the aqueous layer.

We have found that all these processes constituting the prior art either do not result in a clean separation, or are entirely too long and tedious to be commercially useful. So far as we are aware, no process has heretofore been devised by which products of sufficient purity can be obtained from tall oil to meet commercial demands, at a cost sufficiently low to meet market prices of other sources of fatty acids, rosin, etc. In contrast to the processes of the prior art, the process forming the subject of our present application costs little to operate, gives excellent yields, and the final products are of a high degree of purity and commercially useful and valuable.

According to the present invention the separation and recovery of the major components of tall oil, such as fatty acids and resin acids, is effected by an entirely novel method. This method involves a combined process of esterification and solvent extraction. The process is capable of being operated on any mixture or oil comprising resin acids and fatty acids, or crude tall oil, but we prefer to operate on tall oil which has been pretreated and refined in accordance with our copending applications No. 169,655, filed October 18, 1937, and No. 169,656, filed October 18, 1937.

We have taken advantage of the fact that the fatty acids in tall oil may be readily esterified with monohydric alcohols, such as methyl-, ethyl- or higher alcohols, whereas the resin acids remain unchanged. This known chemical principle has

been made the basis of a new and useful process of separation and is an integral part thereof, as hereinafter set forth. That is, the essence of this invention resides in taking together the old process of selective esterification of the fatty acid components carried out under controlled and specified conditions in combination with the new step of subjecting the highly specific esterification mixture to selective solvent extraction.

If a mixture of fatty and resin acids is esterified, the progress of the esterification reaction can be easily followed by the analysis of samples withdrawn at certain intervals of time. For example, on esterifying a tall oil of acid number 166, and containing 50% fatty acids, and 38% resin acids with ethyl alcohol, the following results were obtained:

	Acid number
Original	116
After 15 minutes	87
After 30 minutes	77
After 45 minutes	73
After 60 minutes	72
After 120 minutes	70
After 180 minutes	68
After 240 minutes	68

Assuming complete esterification of the fatty acids, the resin acids (molecular weight 302) should cause the mixture to have an acid number of 67. Thus at the end of 3 to 4 hours the esterification of the fatty acids can be considered complete.

Now, the basis of our precise separation of tall oil constituents resides in the fact we have discovered that after the fatty acids are esterified it is possible by the process disclosed herein to successively extract first the fatty acid ester, and then the resin acid component with a preciseness never before obtained by formerly known methods.

The first step of our process contemplates the esterification of the fatty acids contained in tall oil, which may be effected by several methods, such as refluxing or otherwise reacting the tall oil with a monohydric alcohol such as absolute methyl- or ethyl alcohol, or a higher monohydric alcohol. The alcohol, we find, is preferably used in excess over that required for the quantitative esterification of the fatty acids. Esterification can be effected at or below the boiling point of the esterification mixture in the presence of catalysts, such as sulphuric acid, etc., or by any other conventional or suitable method. After cooling, settling and separation of the sludge formed during the esterification reaction, a strong aqueous solution of an alkali, preferably in excess over that required for the complete neutralization of the resin acids, is added to the solution to neutralize the mixture and form a resin acid soap. Our experiments show that it is important that the concentration of the alkali solution be high enough to cause the formation of a single, homogeneous phase, as no separation into layers of the resin and soap solution and fatty acid ester solution is desired at this point.

Specifically, we have found that the separation of the fatty acid esters from the resin acid soaps is effected very readily with the aid of selective solvents. More specifically, we have discovered that furfural and a hydrocarbon solvent are especially adapted to effect a clean, rapid separation of the fatty acid esters from the resin acid soaps. A hydrocarbon solvent, and as the result of numerous experiments, preferably one of nar-

row boiling range, and furfural are added to the mixture obtained after the neutralization of the resin acids. While furfural and hydrocarbon solvents possess only a limited solubility in each other, no separation of layers will take place when they are added to this mixture as long as the concentration of water is kept low. We thereby obtain a single liquid phase in which all of the components, including both the solvents and the mixture to be extracted, are intimately mixed, and no agitation or raising of the temperature is required to obtain such intimate contact as long as only one layer exists.

Having thus secured an intimate contact of solvents and matter to be extracted, our next step consists of separating the mixture into layers. We have found that on addition of water to the aforementioned mixture, two layers form. The upper, hydrocarbon layer contains the bulk of the fatty acid esters and a portion of the unsaponifiable matter, and the lower layer contains the resin acid soaps dissolved in a mixture of furfural and water. After separating the upper layer, the furfural layer may be extracted one or more times with smaller portions of the hydrocarbon solvent in order to extract any fatty acid esters that may remain in the lower layer as completely as is considered economical. We have found that approximately 90% of the esters are removed by the first extraction, and three or four extractions with smaller portions of hydrocarbon solvent will remove substantially all of the fatty acid esters from the furfural layer. We also find it desirable to wash the hydrocarbon solutions of the fatty acid esters with small quantities of water in order to remove most of the furfural dissolved in the hydrocarbon.

Among the numerous and valuable advantages of this process is the clean, rapid separation of the fatty acid esters from the resin acid soaps. When water containing a considerable proportion of alcohol is employed as a solvent for the resin acid soaps, and the esters are taken up by a hydrocarbon solvent as in the gravimetric analytical method for the determination of resin acids, invariably the hydrocarbon solvent dissolves a portion of the soap which has to be removed by protracted washing. As mentioned in the discussion of the prior art, this procedure also leads to the formation of troublesome emulsions which make operation on a large scale unfeasible. These disadvantages are, for the first time, successfully avoided in our process. We find, moreover the retentive power of the furfural-water mixture for resin acid soaps is so great that no resin acid soap will be found in the hydrocarbon-ester layer. It is also of eminent practical importance that no emulsions are formed during the course of the extraction. In our process, the separation of the hydrocarbon and the furfural layers is extremely rapid, and a sharp separation into layers takes place within a few minutes.

These hydrocarbon solutions are then subjected to distillation, preferably with steam to remove the hydrocarbon and any residual small quantity of furfural. The fatty acid esters so obtained from our improved process are of a light yellow color and contain approximately one-half of the unsaponifiable matter originally present in the tall oil. In our process, the esters can be purified and obtained substantially free from unsaponifiable matter by distillation, the

unsaponifiable portion remaining in the still residue.

The esters so obtained by our process are either used industrially as starting materials for fatty acid derivatives, or are subjected to splitting or saponification by well known methods such as hydrolysis by the Twitchell process, or splitting by the autoclave process, or saponification with sodium hydroxide and subsequent liberation of the fatty acids. It is, therefore, clear to those skilled in the art that fatty acids free of resin acids are thus obtained by a direct and simple process not previously known or practiced.

The next major step in our inventive procedure consists of the recovery of the resin acids from their soaps contained in the furfural-water solution. This is effected by adding the theoretical amount of acid, preferably but not necessarily a mineral acid, to the furfural water layer to liberate the resin acids from their soaps, and extracting the resin acids with a hydrocarbon solvent. By distilling off the solvent and any furfural dissolved therein, resin acids of light yellow color are obtained.

The furfural is then subsequently recovered from the furfural-water mixture left after the extraction of the resin acids by steam distillation or by any other convenient method, and the still residue left after the distillation of furfural is a dark colored, brittle, resinous substance which contains a small proportion of resin acids, some unsaponifiable matter and practically all of the coloring matter of tall oil.

A great advantage of our method, and a necessary requirement for practical and economical operation, is that the materials involved in the esterification and extraction procedures, such as excess alcohol and solvents, be capable of being completely recovered by very simple and economical methods such as by distillation. Our experiments show that about one-fourth of the excess alcohol is contained in the sludge separated after the esterification. Other than this, it can be seen that the balance of the excess alcohol can be recovered by distillation of the esterified mixture before subjecting it to solvent extraction, or may be recovered together with the furfural at the end of the process.

The following examples will illustrate our process, although we do not limit ourselves to the conditions as disclosed in these particular examples:

Example I

Three kilograms of tall oil containing 50% fatty acids, 40% resin acids, 10% unsaponifiable and coloring matter, are mixed with 600 cc. of ethyl alcohol and 100 grams of sulphuric acid. The mixture is refluxed for four hours and let stand to settle. The sludge which is drawn off contains water, 70% of the sulphuric acid added, and 70 cc. of alcohol. The esterified mixture is treated with 350 cc. of a sodium hydroxide solution containing 175 grams of sodium hydroxide. Three liters of naphtha and one and one-half liter of furfural are now added and the mixture lightly stirred until a homogeneous solution results. On adding 2.5 liters of water two layers are obtained, namely 4.85 liters of an upper, light yellow naphtha layer, and a larger volume of a lower, dark brown furfural layer. The latter is extracted twice more with 800 cc. and 400 cc. naphtha respectively, and the resulting upper layers (900 cc. and 420 cc.) separated. The united naphtha layers are washed

with small quantities of water, and the naphtha distilled off preferably by steam. A clear, light yellow liquid (1.79 kg.) is obtained as residue representing the fatty acid esters and a few percent of unsaponifiable matter. To the furfural-water layer, sufficient dilute sulphuric acid is now added to liberate the resin acids from their soaps and the resin acids extracted with three liters, and subsequently with smaller quantities of naphtha. The united naphtha solutions of the resin acids are distilled to remove the naphtha and the dissolved furfural. Light colored resin acids are obtained (1.15 kg.). On distilling the residual furfural-water layer 200 cc. of alcohol and the furfural are recovered, and as a residue 200 gms. of a mixture of unsaponifiable, resin acids and coloring matter are obtained.

Example II

One kilogram of tall oil from a Southern coniferous wood source, was refined according to our processes disclosed in our co-pending applications No. 169,655 and No. 169,656, from which we obtained 927 grams of a refined oil of light yellow color as our starting point. Nine hundred grams of this refined oil are reacted by refluxing with 376 cc. absolute alcohol in the presence of 33 grams sulfuric acid. After neutralizing the sulfuric acid, the excess alcohol is recovered by distillation and we obtain 933 grams of the esterified mixture having an acid number of 71. The resin acids in this mixture are now neutralized with 120 cc. of a solution containing 48 grams sodium hydroxide. Addition of 1000 cc. of naphtha and 500 cc. of furfural causes the formation of a single phase, which on adding 600 cc. water separates into two layers. After removing the naphtha-ester layer, the extraction is repeated twice with smaller quantities of naphtha. The resin acids are liberated from their soaps contained in the furfural layer by adding 150 cc. of 8 N. sulfuric acid, and the resin acids are extracted from the furfural-water layer with several portions of naphtha. Distillation of the naphtha solutions yields 546 grams esters and 299 grams resin acids respectively. Both esters and resin acids contain a small proportion of unsaponifiable matter. Distillation of the furfural-water mixture yields 70 grams of a dark colored brittle substance composed mainly of resin acids.

We claim as our invention:

1. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and treating the neutralized esterification mixture with two organic solvents and water, said solvents being substantially immiscible in each other and separable into two layers upon the addition of water, whereby the fatty acid esters are precisely dissolved in only one of the organic solvents.

2. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and treating the neutralized esterification mixture with two organic solvents and water, said solvents being substantially immiscible in each other and separable into two layers upon the addition of water, whereby the fatty acid esters are precisely dissolved in only one of the organic solvents, and resin acid soaps are dissolved only in the other solvent.

3. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and treating the neutralized esterification mixture with two

organic solvents, said solvents being substantially immiscible in each other and separable into two layers upon the addition of water, and then causing the separation of said solvent solution into two layers by the addition of water, whereby the fatty acid esters are precisely dissolved in only one of the organic solvents, and resin acid soaps are dissolved only in the other solvent.

4. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and treating the neutralized esterification mixture with two organic solvents and water, said solvents being substantially immiscible in each other and separable into two layers upon the addition of water, whereby the fatty acid esters are precisely dissolved in only one of the organic solvents, and resin acid soaps are dissolved only in the other solvent, the said solvent solutions being formed into two layers, and separately recovering the respective constituents of said solvent solution layers.

5. The process of separating fatty acids from resin acids, which comprises the esterification of the fatty acids with a monohydric alcohol, neutralizing the mixture and treating the neutralized esterification mixture with two organic solvents and water, said solvents being substantially immiscible in each other and separable into two layers upon the addition of water, whereby the fatty acid esters are precisely dissolved in only one of the organic solvents.

6. The process of separating fatty acids from resin acids, which comprises the esterification of the fatty acids with a monohydric alcohol, neutralizing the mixture, and treating the neutralized esterification mixture with a hydrocarbon solvent, furfural and water, whereby the fatty acid esters are precisely dissolved into only the hydrocarbon solvent.

7. The process of separating fatty acids from resin acids, which comprises the esterification of the fatty acids with a monohydric alcohol, neutralizing the mixture, and treating the neutralized esterification mixture with a hydrocarbon solvent, furfural and water, whereby the fatty acid esters are precisely dissolved into only the hydrocarbon solvent, and the resin acid soaps are precisely dissolved into only the furfural and water.

8. The process of separating fatty acids from resin acids, which comprises the esterification of the fatty acids with a monohydric alcohol, neutralizing the mixture, and treating the neutralized esterification mixture with a hydrocarbon solvent and furfural, thereby forming a single homogeneous liquid phase, and adding water thereto to cause a separation of said mixture into two solvent solution layers, and separately recovering the respective constituent compounds of said layers.

9. The process of separating fatty acid esters from resin acid soaps in mixtures thereof which comprises treating the mixture with a hydrocarbon solvent, furfural and water.

10. The process of separating fatty acid esters from resin acid soaps in mixtures thereof, which comprises treating the mixture with a hydro-

carbon solvent and furfural, adding water to cause a separation into layers, and decanting the layers apart.

11. In the process of separation of fatty acids from resin acids the step which comprises the formation of a two-phase liquid system, comprising an upper layer of a hydrocarbon solvent and monohydric alcohol esters of tall oil fatty acids, and a lower layer of furfural; water and resin acid soaps.

12. In the process of separation of fatty acids from resin acids the step which comprises the formation of a two-phase liquid system, comprising an upper layer of a hydrocarbon solvent and monohydric alcohol esters of tall oil fatty acids substantially free of resin acid compounds and a lower layer of furfural; water and resin acid soaps substantially free of fatty acid compounds.

13. In the process of separation of fatty acids from resin acids the step which comprises the formation of a two-phase liquid system, comprising an upper layer of a hydrocarbon solvent and monohydric alcohol esters of mixed fatty acids and a lower layer of furfural; water and resin acid soaps.

14. In the process of separation of fatty acids from resin acids the step which comprises the formation of a two-phase liquid system, comprising an upper layer of a hydrocarbon solvent and monohydric alcohol esters of mixed fatty acids substantially free of resin acid compounds and a lower layer of furfural, water and resin acid soaps substantially free of fatty acid compounds.

15. The process of separating and recovering fatty acids and resin acids from their mixtures, which comprises esterifying the fatty acids in said mixture by means of a monohydric alcohol and an esterification catalyst, adding an aqueous alkaline solution to said mixture to neutralize it and to form a homogeneous mixture comprising resin acid soap and fatty acid ester, adding thereto furfural and a hydrocarbon solvent to form a homogeneous mixture, adding an excess of water to form an upper layer of essentially fatty acid esters in hydrocarbon solvent, and a lower layer of essentially resin acid soap in furfural, separating the said layers by decantation, and recovering therefrom respectively fatty acids and resin acids.

16. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and differentially dissolving the fatty acid esters in one solvent and dissolving the resin acid soaps in another solvent which is substantially immiscible with the first solvent.

17. The process of separating fatty acids from resin acids, comprising esterifying the fatty acids, neutralizing the resultant mixture and differentially dissolving the fatty acid esters in one solvent and dissolving the resin acid soaps in another solvent which becomes substantially immiscible with the first solvent on the addition of water.

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