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PROCESS FOR SEPARATING UNSAPONIFIABLE COMPOUNDS FROM OXIDATION PRODUCTS OF HIGHER MOLECULAR HYDROCARBONS

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This invention relates to a process for separating unsaponifiable compounds from oxidation products of higher molecular hydrocarbons.

The oxidation of higher molecular hydrocarbons, such as paraffingatsch, is directed in such a manner that the products, besides fatty acids and similar compounds, contain considerable quantities of unsaponifiable hydrocarbons which may amount to 60% and more. It is known to separate unsaponifiable compounds from the oxidation products by destilling after saponification of the fatty acids, etc. the volatile constituents from the soaps. Before or after separation of the unsaponifiable compounds, which may be effected of course by other methods than distillation, the fatty acids have also been saponified and then heated up to approximately 280–350° C. so as to convert oxyacids, lactones lactides, estolides and other polymeric esters formed in oxidation into fatty acids. In this known procedure heating required approximately 1 to 10 hours, depending on the treating temperature.

It is further known to remove volatile constituents from aqueous saponification products of synthetic or natural fatty acids by heating the saponification products under pressure beyond the melting point of the anhydrous soaps. At the same or a still higher temperature, possibly while reducing pressure in vacuo or supplying water vapor or inert gases, the water and the unsaponifiable portions or the other volatile constituents are driven out by distillation.

The known processes combining with the removal by distillation of the unsaponifiable and other volatile substances an improvement of the saponified fatty acids apply high pressures and require therefore expensive apparatus of relatively low output.

It is an object of invention to eliminate these disadvantages for this purpose: The oxidation products of higher molecular, particular aliphatic, hydrocarbons, as paraffingatsch, etc., are first saponified, whereupon the mixture of fatty acid soaps and unsaponifiable substances is freed from water and then heated up to about 310–350° C. The absolute pressure at which this treatment is performed is so adjusted that only a portion of the unsaponifiable substances is removed by distillation, and the heating is continued as long as required for converting the oxyacids, lactones etc. Then the remainder of the unsaponifiable substances is distilled off whereby the temperature may be lowered and the pressure reduced to vacuum, preferably high vacuum. The treatment according to the invention is preferably combined with intensive motion, for instance by rotating the liquid or melt in the vessels and/or passing steam therethrough.

It has been found that the soap melt as long as it contains the unsaponifiable substances or a portion thereof remains in a thinly liquid state and withstands temperatures up to about 350° C and over without injury, so that the process according to the invention yields, a carefully preserved fatty acid of high grade. Owing to the possibility afforded by the invention of removing by distillation a part of the unsaponifiable substances already during the step of heating to high temperatures, these steps of the treatment as well as the following ones may be carried out at greater efficiency. Furthermore, the treating period is shortened, since while heating to high temperatures is going on a portion of the unsaponifiable substances can be distilled off and the removal by distillation of the remaining portion may be effected immediately after heating. Finally, as part of the considerable amount of heat still retained by the highly heated melt is utilized for distilling off the unsaponifiable substances, the heat economy is generally improved.

If on the other hand according to known methods the dry molten soap is highly heated in the absence of diluents and kept for the necessary time at the high temperatures required for improving fatty acids, uneven heating as well as local overheating of the soaps is unavoidable with the result that the soaps are injured by partial decomposition. The yield of fatty acids and the color thereof are particularly affected.

When in the process according to the invention, after the refinement of the fatty acids, the unsaponifiable substances are distilled off in a high vacuum, the temperature of distillation may be correspondingly reduced, whereby the soap melt from which the unsaponifiable substances are more and more withdrawn during distillation and which thus becomes more sensitive to high temperatures is preserved still more. After the unsaponifiable substances have been removed by distillation the temperature of the soap melt is reduced in known manner, for instance by passing therethrough low pressure steam or injecting water, but the temperature must still be high enough to permit removal of the soap in thinly liquid condition from the apparatus. It is further possible to place the soap after completion of distillation in a vacuumized autoclave equipped with agitators and heating means and then to eliminate the vacuum by steam developed for instance from introduced water. By the further

supply of water to the autoclave, for instance under pressure, the melt can be converted into an aqueous soap, the temperature of which may be correspondingly reduced, the pressure in the autoclave being easily regulatable by blowing off steam. The liquid soap can then be conveyed to a plant in which the soaps are decomposed, for instance by adding mineral acid, and the liberated fatty acid after having been washed with water, etc. in the usual way is worked in a high vacuum distillation apparatus. The distillates obtained are of high grade and have a light color.

Example 1

Paraffingatsch obtained by the Fischer-Tropsch-synthesis from carbonmonoxide and hydrogen is oxidised in known manner to crude fatty acids which contained considerable portions of unoxidised or partly oxidised products. To the products of the oxidation the quantity for sodium carbonate solution of 30° Bé. theoretically required for the saponification of the fatty acids contained in the products is added in an autoclave provided with agitator and heating means. After the sodium carbonate solution has acted upon the fatty acids, soda lye of 40° Bé. to the extent of 10% of the amount of alkali theoretically required for saponification is added and while the contents of the autoclave are heated saponification is completed at a pressure of 7 atmospheres. The mixture of fatty acid soaps and unsaponifiable substances kept liquid by corresponding heating is then dehydrated under pressure, whereupon the molten mixture is placed in a distilling vessel equipped with heating means, agitators and steam spray and heated therein in vacuo up to about 335° C while it is thoroughly stirred and water vapor passed through it. This temperature is maintained for two hours and the vacuum so adjusted that during heating and the conversion of the oxyacids, lactones etc. to fatty acids approximately one-half of the unsaponifiable substances is distilled off, chiefly the lower boiling portions of the distillable substances present passing over.

The mixture treated as described had been obtained by the oxidation of crude paraffin boiling between 320° and 450° C. The content of acid oxidation products of the mixture amounts to approximately 40%.

While the mixture is heated up to about 335° C the presence of the unsaponifiable substances has the effect of keeping it in thinly liquid condition, so that uniform heating is insured and local overheating or decomposition of the molten mixture cannot occur. After the fatty acids have been refined by heating the steam is shut off and a high vacuum gradually produced in the distilling vessel, so that everything distillable still present in the mixture is driven off. Owing to distillation the temperature of the contents of the vessel is lowered. When it has reached about 290° C, heating is started again and distillation completed at this temperature. The soap melt is then placed in a vacuumized vessel provided with agitator and heating means and constructed as autoclave. Into the soap melt water is introduced, f. i. by a pump, until the water vapor produced has destroyed the vacuum and a pressure regulatable at will by blowing off vapor develops in the autoclave. The soap melt absorbs water and gradually changes into an aqueous liquid soap while its temperature is considerably reduced. From the autoclave the soap solution is passed to another plant in which it is decomposed by sulfuric acid, whereupon the fatty acid so produced can be distilled in known manner.

Example 2

Starting material of the kind referred to in Example 1 is mixed in a similar saponifying apparatus with the requisite amount of 40° soda lye and simultaneously heated. The steam pressure developing in the autoclave is kept at 5 atmospheres. After the saponification of the fatty acids the mixture of soap and unsaponifiable constituents is sucked into a vacuumized distilling apparatus provided with heating means, stirring device and steam spray, the stirrer being in operation during suction. While the mixture is being drawn in, the main part of the water contained in the soap is evaporated. When the heating coil is covered with the mixture of soap and unsaponifiable constituents, the heating is turned on and superheated steam passed through the spray. A short time after having been sucked in, which requires about 15 minutes, the mixture is free from water and by continual stirring and the passage of water vapor is brought to a temperature of 325° C. The vacuum is so adjusted that during heating and the consequent conversion of the oxyacids, lactones, etc. into fatty acids only one-third of the unsaponifiable constituents is distilled off which comprise the lower boiling substances. The contents of the distilling apparatus are kept at a temperature of 325° C. for 3 hours, and the presence of the unsaponifiable constituents has here the same good effect as in Example 1. After refining the unsaponifiable constituents still present are distilled off as described in Example 1, and the soap melt is drained into a vacuumized outfit provided with stirrer, heating means and steam spray, whereupon it is stirred and low pressure steam passed through it to eliminate the vacuum, and at a steam pressure of half an atmosphere the temperature of the soap melt is reduced to 250–260° C. The soap is then drawn off over a cooling roller or placed in an apparatus wherein it is continuously decomposed into fatty acid and Glauber's salt solution with the aid of sulfuric acid.

Example 3

The procedure was the same as described in Examples 1 and 2, though instead of the sodium compounds mentioned the corresponding potassium compounds were used for saponification, so that after refining and distilling off the unsaponifiable constituents the soap melt could be cooled down to 150° C. and was found to be still liquid.

Similar advantages are obtainable if saponification is performed with mixtures of sodium and potassium compounds.

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