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PROCESS FOR SEPARATING UNSAPONIFIABLE SUBSTANCES FROM THEIR MIXTURES OR COMPOUNDS WITH SAPONIFIABLE SUBSTANCES

Hermann Pardun, Hamburg-Harburg, Germany, assignor to the firm Noblee & Thörl G. m. b. H., Hamburg-Harburg, Germany

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This invention concerns a process for separating unsaponifiable substances from their mixtures or compounds with saponifiable substances.

It is already known to separate unsaponifiable bodies from their mixtures or compounds with natural or synthetic fatty acids by way of saponification with aqueous alkalihydroxydes and distillation of the saponification products. In consequence of their considerably free lathering properties aqueous soap solutions are not suitable for subjection to a normal distillation. Until now only two ways existed to separate soaps from unsaponifiable matter.

On a cylinder drying machine the soap is thickened by evaporation until it is dry. The dry mass is melted in a distillation vessel and freed from unsaponifiable matter by distillation at normal pressure or by vacuum, if desired by steam distillation. This process is, however, owing to the protracted drying of the suds, very expensive. When the dry soap is heated to its melting point a decomposition is caused by local overheating, which means another disadvantage of the predescribed process.

Consequently one had to withdraw from a preceding drying of the soap. According to another method the aqueous soap solution is heated in a pressure vessel up to a temperature and a pressure, at which, after relaxation, the unsaponifiable is carried away with the vapours which are clearing off. The soap is retained in molten condition. Although this method helps to avoid disadvantages of the first method, working at high temperatures and pressures, for example at 300° C. and 100 atm. and a large and expensive apparatus are rendered necessary.

According to the invention it has been found that by a much simpler method mixtures or compounds containing saponifiable substances may be freed from unsaponifiable parts by injecting an aqueous product obtained by saponification with aqueous alkaline agents into a molten mass of soap thus freeing the saponification products from water and a part of unsaponifiable matter and then distilling off the remaining unsaponifiable parts in high vacuum, preferably below 2 mm. Hg, if desired by help of indifferent gases or steams, from the obtained molten anhydrous soap.

The process is mainly suitable for depriving the intermediates obtained by oxydation of higher molecular aliphatic or cycloaliphatic hydrocarbons of the unsaponifiable bodies. The kind of oxydation as well as origin and quality of the starting material to be oxydised are unimportant. Soft and hard paraffine from natural raw material, for example earth oil distillates, as well as higher molecular products, obtained by various methods for the production of synthetic hydrocarbons, as for example hydrogenation products of carbonmonoxide with a distillation temperature over 250° C. (so-called Fischer-Tropsch-Gatsch) may be used as starting materials for oxydation. They may be oxydised with free or combined oxygen.

The present method may also be used successfully for freeing natural fats, such as sperm oil, wool fat, fat wastes as well as waxes and mixtures obtained by the reduction of higher molecular fatty acids to fatty alcohols, from unsaponifiable bodies.

In order to prepare the aqueous saponification products, these starting materials are saponified with alkaline agents, for example hydroxydes and carbonates of alkalis and hydroxydes of earths alkaline and earth metals, as well as such organic bases, the fatty acid salts of which do not decompose at the melting temperature used. Appropriately the concentration of the saponifying agents should be such that soap solutions of about 30–50% are obtained. Saponification may take place at normal or higher pressure. The presence of organic, water soluble solvents as low molecular alcohols is of no harm. Sometimes their presence is advantageous for example with the saponification of waxes. Saponification products prepared accordingly may be deprived of that unsaponifiable part eliminated by itself in known mechanical manner before the treatment according to the invention.

In carrying out the process a small amount of soap dried in the usual way is put into a closed vessel which can be heated and is equipped with charging means for the aqueous saponification product and outlets for the arising gases and steams produced. By careful rises in temperature the soap is melted. The rise in temperature is increased until a fluid liquid is obtained. The working temperatures are ranging between 200 and 400° C., preferably between 275 and 325° C. according to the kind of starting material to be used. The presence of unsaponifiable bodies prevents undesirable decompositions arising in the range of these temperatures and further prevents the dangerous incrustation of the vessel from taking place. Larger vessels being used it is advantageous to keep the molten material in perpetual move by an agitator or steam blowing apparatus.

A thin steam of the prepared aqueous saponi-

fication product is injected into the molten mass by help of a distributor, a nozzle or the like. The velocity of the flow is adjusted according to the amount of warmth available in the evaporator. When brought into contact with the molten mass the water and a part of unsaponifiable matter are evaporating. The soap immediately turns into a molten condition without any visible intermediate step. After, if desired, the amount of warmth contained in the steam and the unsaponifiable body is rendered profitable, these are led into a condensator in which two layers are formed, the top one of which consists of the unsaponifiable body, the bottom one of water and the organic solvent, which may have been used. By blowing over-heated steam into the melt or by use of a low vacuum the process may be considerably accelerated.

The so obtained molten soap still contains a considerable amount of unsaponifiable bodies, ranging according to the working temperature. It is freed from the rest of the unsaponifiable matter in known manner by distillation in high vacuum in the same or another vessel, preferably at a pressure below 2 mm. Hg. Since in the preceding working step the water and the easily volatilizing parts of the unsaponifiable body have been completely removed distillation takes place spontaneously at a temperature of from 200° C. to 400° C. and is finished within a few minutes. In order to accelerate the process of distilling off indifferent gases or steams may be introduced in usual manner. The heating of the soap according to the invention is so short that a deleterious effect on the soap is avoided. The removal of the unsaponifiable body practically takes place without any losses. The obtained molten soap is discharged, moulded, sliced, cut into chips or pulverized and is ready for use.

The process may be carried into effect continuously or discontinuously.

Working discontinuously a distillation still of usual construction is made use of. This shows the simplicity of the whole apparatus. The still is furnished with aqueous saponifying products in the predescribed manner until it is filled half way after which high vacuum is commuted. When the distillation is finished the still's content is emptied out except for a small quantity, into which suds are injected afresh.

It is, however, more advisable to make use of the continuous process, the time of reaction during both steps of the process being very short. In carrying out this process in a simple manner two distillation vessels, which have been connected with each other, are floated by the material to be distilled consecutively. The product, which in the first vessel has been freed from water and the main part of the unsaponifiable body is discharged continuously into a second distillation apparatus which is kept under high vacuum. Here it is deprived from the rest of unsaponifiable body and is flowing into a suitable receptacle from which it is withdrawn continuously. During the second step a known device is used with advantage in which the molten soap is led in a thin film over heated guiding plates, tubes and the like. Thus on the one hand a good transference of the warmth is guaranteed, even if the molten soap, after having been freed from unsaponifiable matter, is hardly fusible. On the other hand the evaporation of unsaponifiable matter does take place a good deal quicker than it would in an ordinary distillation still.

In case fractionation of unsaponifiable matter obtained during the second step is desired, this is easily brought about by arranging several heating systems heated to different temperatures and separate withdrawal of the arising steams.

The predescribed process of separating unsaponifiable parts may be combined with bleaching in order to obtain light soaps. For this purpose reducing or oxydising agents may be added to the aqueous mass of soap, which agents in the first or second step are causing a bleaching of the soap.

Agents such as salts of organic or unorganic acids, which reduce the melting point of soap may be added.

By the present process unsaponifiable matter, except for a small rest, is removed. This rest is of no practical importance, especially in view of the fact that in general the obtained soaps are worked up with mineral acids and the liberated fatty acids are distilled off, during which distillation the rest of unsaponifiable body remains in the residue.

It is, however, also possible to purify the obtained product afterwards in known manner with the aid of extracting agents, such as benzin, benzene, alcohol, acetone and the like in order to remove the very rest of the unsaponifiable matter.

According to the present invention light coloured unsaponifiable and soaps with free lathering properties are obtained. The fatty acids obtained from the soaps may, if desired after distillation, be used in known manner for industrial purposes, for example in the soap industry.

Examples

1. 20 parts of a product with an acid value of 139 and a saponification value of 173 obtained by oxydising hydrogenation products of carbonmonoxide with a distillation temperature over 250° C. (so-called Fischer-Tropsch-Gatsch) at a temperature of 120° C. were saponified with a 30% aqueous sodium hydroxyde lye an excess of 5% being added. The mass carefully evaporated to dryness was heated up to 275° C. in an indirectly heated distillation vessel until a fluid melt was obtained. Now a soap solution, prepared from 160 parts of same oxydation product and a 15% sodium hydroxyde lye in an excess of 5%, was injected into the melt. Water and the greatest part of unsaponifiable matter volatilized without any disturbing foam or drops arising. Water and 46 parts of unsaponifiable matter gathered in a receiver. The aflux of the soapy solution was stopped, the temperature raised to 325° C. and the rest of unsaponifiable distilled off in vacuum of 1 mm. Hg. The supply with small quantities of over-heated vapour sufficed to cause a revolution of the distillation product. After a quarter of an hour unsaponifiable matter had completely vanished. The molten soap solidified on a cooling drum and turned a light brown mass. Fatty acids obtained by acidifying mineral acids were practically free from unsaponifiable matter and had the following values: Acid value 237; saponification value 258; OH value 13. 56 parts unsaponifiable matter of light colour with the following values:

Acid value 1; saponification value 40; OH value 54 were obtained from both steps together.

2. 20 parts of a product showing an acid value of 106 and a saponification value of 152 obtained from hard paraffine with the melting point of 54° C. by oxydation at 140° C. were saponified for 1 hour at 150° C. with a calculated quantity of 30% sodium hydroxide lye an excess of 5% being

added. The prepared soapy mass was dried and molten in a distillation vessel equipped with an outlet for the molten soap. By way of a nozzle arrangement capable of supplying the whole surface of the molten product a soapy solution, obtained by saponifying 180 parts of same oxydation product with 15% sodium hydroxide lye was added in the course of one hour at a temperature of 300° C. Water and a part of unsaponifiable evaporated and were condensed in usual manner.

During the injection of the sud the melt is continuously emptied out. In a device constructed according to the so called short way distillation a thin film of the melt is heated to 350° C. under a vacuum of 1 mm. Hg. Within a few minutes the rest of unsaponifiable evaporated. The molten soap, practically containing no more of unsaponifiable matter, was pumped from the apparatus.

71 parts firm unsaponifiable of light colour resulted in total. Fatty acids obtained from soap by acidifying with mineral acid yielded after distillation white, firm products, which do not differ much from natural fatty acids.

3. 10 parts sperm oil having an acid value of 0.9 and a saponification value of 141 were, after the addition of 3.5 parts 30% sodium hydroxide lye and 10 parts ethyl alcohol, saponified for one hour. 190 parts of same sperm oil saponified with 66.5 parts of 30% sodium lye and 50 parts of alcohol in order to obtain a homogenous liquid were injected into the dry and molten saponification product in the course of 2 hours. Together with water and ethyl alcohol 34 parts of sperm oil alcohols distilled off at 320° C., the sperm oil alcohols gathering as a yellow oil on the aqueous solution.

During repeated distillation under high vacuum of 1 mm. Hg and at a temperature of 300° C. the resulting soap melt yielded another 42 parts of unsaponifiable matter.

The united unsaponifiable parts represented a mixture of almost pure higher molecular alcohols of the following values:

Acid value 1; saponification value 29; OH value 482.

The fatty acids obtained from the soap melt were of a light colour and contained 2% of unsaponifiable matter.

What I claim is:

1. In a process for separating mixtures of compounds of unsaponifiable and saponifiable matter, the step of saponifying such mixture or compound with an aqueous solution of a basic agent, melting anhydrous soap, injecting the aqueous saponification product into the molten soap, whereby water and a portion of unsaponifiable matter are removed and the molten soap becomes anhydrous, and distilling off the remainder of the unsaponifiable matter from this soap in high vacuum.

2. Process according to claim 1, wherein the aqueous saponification product is injected into the molten soap at temperatures ranging between 200° C. and 400° C.

3. Process according to claim 1, wherein the aqueous saponification product is injected into the molten soap at temperatures ranging between 270° C. and 325° C.

4. Process according to claim 1, wherein before the injection a water soluble low molecular alcohol is added to the aqueous saponification product.

5. Process according to claim 1, wherein the remainder of the unsaponifiable matter is distilled off from the anhydrous soap under pressures below 2 mm. Hg.

6. Process according to claim 1, wherein the remainder of the unsaponifiable matter is distilled off from the anhydrous soap in the presence of an inert gas.

7. Process according to claim 1, wherein the soap after having been freed from the remainder of the unsaponifiable matter is treated with an organic solvent selected from the group consisting of benzine, benzene, alcohol and acetone.

HERMANN PARDUN.