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PATENT SPECIFICATION

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487,317

PROVISIONAL SPECIFICATION
No. 30937 A.D. 1936.

A Process for Improving Soaps from Oxidation Products of Non-aromatic Hydrocarbons of High Molecular Weight and Apparatus therefor

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

In the preparation of soaps from oxidation products of non-aromatic hydrocarbons of high molecular weight, as for example paraffin wax, it is necessary that the saponification products should be substantially free from hydroxy fatty acids, lactones and the like as well as from polymeric constituents because these substances impart to the soaps an unpleasant odour and cause undesirable discolouration so that they are unsuitable for many purposes, as for example for domestic use.

My foreign correspondents have now found that soaps from oxidation products of non-aromatic hydrocarbons of high molecular weight which are free from hydroxy acids, lactones and the like can be obtained in a simple manner by heating the saponified oxidation product together with at least an equal amount by weight of water calculated on the anhydrous crude saponified product to temperatures above 300° Centigrade under increased pressure.

As initial materials for the said process there may be mentioned oxidation products of hard and soft paraffin wax, paraffin oil, petroleum, and non-aromatic hydrogenation products of coal, tars and the like. In the present case products may be used which have been obtained by saponification of the oxidation products with amounts of alkalies which correspond to the saponification value or which are somewhat larger or smaller than the said amount. It is advantageous to use saponification products having a water content of at least 150 per cent. calculated on the soaps contained therein. The duration of the treatment depends in general on the nature of the oxidation products, for example on their content of hydroxy fatty acids, lactones and the like. As a rule it is necessary to carry on the heat treatment for at least an hour. The most favourable temperatures for the process according to this invention lie between 310° and 350° Centigrade and it is advantageous to work at about 320° Centigrade. The pressure amounts to about 100 atmospheres or more.

It is especially preferable to release the pressure on the saponification mixture heated under pressure, the said release of pressure being effected while further heating the mixture, whereby the unsaponifiable constituents are removed with the steam. The release of pressure is advantageously effected in stages, by which means it is ensured that the soap remains as long as possible in aqueous solution and sufficient steam is present for the removal of the whole of the unsaponifiable constituents. It is preferable first to release the pressure, by suitable regulation of valves, to a pressure of from 20 to 50 atmospheres; however, the temperature of the saponification product which is lowered by the release of pressure is raised again to from 320° to 330° Centigrade. Heating to the said temperature is also necessary for the further release of pressure to atmospheric pressure.

The unsaponifiable constituents which distil off with the steam may be recovered by condensation and if desired subjected again to oxidation together with fresh paraffin wax or the like. The soaps are obtained in an anhydrous, fused state and may be worked up into soap powder or grain soap after cooling and comminution.

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Price

The process is preferably carried out continuously and the accompanying drawing illustrates an example of apparatus suitable for continuous operation; the invention is, however, not restricted to the particular example of apparatus shewn.

Referring to Figure 1 of the drawing, 1 is a measuring vessel for the oxidation product, 2 is a measuring vessel for the caustic soda solution, 3 is a stirring vessel with a drain pipe 5 for the unsaponifiable material, 6 is a filter, 7 is a high-pressure pump, 8 is a check valve, 9 a reaction chamber, 10 and 11 are pressure-release valves, 12 an inlet for the heating gases, 13 an outlet pipe for the waste gases, 14 a collecting vessel for the fused soap, 15 a cooling roller, 16 a cooler for the unsaponifiable constituents and steam, 17 a separating vessel for the unsaponifiable constituents, 18 a drain pipe for the condensed water, 19 a drain pipe for the unsaponifiable constituents and 20, 21 and 22 are manometers.

The following Examples, given with reference to the drawing, will further illustrate the nature of this invention, but the invention is not restricted to these Examples.

Example 1.

A product obtained by the oxidation of hard paraffin wax in the liquid phase by leading in air at 150° Centigrade with an addition of manganese naphthenate as catalyst, is intimately mixed with a 20 per cent. solution of caustic soda, at 90° Centigrade in the stirring vessel 3, in an amount containing 4 per cent. of caustic soda less than corresponds to the theoretically necessary amount for the complete saponification of the fatty acids and esters. Water is added to the saponification mixture in such an amount that in all 70 per cent. of water are contained therein. The unsaponifiable constituents separate as the top layer on standing; they are withdrawn through the drain pipe 5 after the lower layer has left the stirring vessel at its bottom and before new oxidation product is introduced into this vessel. The soap solution is pumped through the filter 6 with the aid of the high-pressure pump 7 and through the check valve 8 into a reaction chamber 9 consisting of a tube system and heated therein to from 310° to 320° Centigrade; the speed of flow is regulated so that a pressure of 160 atmospheres is set up and the saponification mixture remains in the chamber for about 2 hours. The uniform maintenance of the pressure is regulated by the release valve 10. The pressure is then released in stages, the first stage being by means of the valve 10 from 160 to 25 atmospheres. With the effluent vapours, a part of the unsaponifiable material is removed from the saponification mixture. The saponification mixture is then released to atmospheric pressure by a second valve 11, whereby the unsaponifiable constituents as well as coloured constituents and odorous substances are practically completely removed with the steam.

The remaining soap melt is pale in colour. It is led into the collecting vessel 14 and passes thence to a cooling roller 15 on which it is worked up into flakes. The steam with the unsaponifiable constituents passes through the collecting vessel 14 into the cooler 16 in which the condensation takes place. The unsaponifiable constituents are collected in the separation vessel 17 and supplied to the oxidation again through the drain pipe 19. The condensed water may be removed through the drain pipe 18.

The crude soap obtained is dissolved in water and then acidified with dilute sulphuric acid. The crude acids thus separated, which contain only from 0.5 to 1 per cent. of unsaponifiable constituents, are distilled with steam under a pressure of 2 millimetres (mercury gauge). The following results are thus obtained:—

Distillation residue	Ester value of the fatty acids	Colour of the fatty acids in the 1 inch trough of the Lovibond Tintometer red
18 per cent.	0	1.0

The fatty acids obtained are free from lactones, hydroxy acids and the like and have a very pale colour.

Example 2.

400 parts of an oxidation product having a saponification value of 146 (obtained by the oxidation of hard paraffin wax with air at 115° Centigrade with an addition of sodium palmitate as catalyst) are, after the addition of 200 parts of water and 116 parts of 35 per cent. caustic soda solution, saponified. After allowing to stand for a short time, a part of the unsaponifiable constituents separates on the surface of the same and is removed, the saponification mixture then being

introduced into the reaction chamber shewn in the drawing, and heated to 315° Centigrade. After treatment for $1\frac{1}{2}$ hours under a pressure of 150 atmospheres, the saponification mixture is released to a pressure of 30 atmospheres, the major portion of the unsaponifiable constituents being removed with the effluent steam. As soon as the saponification mixture has again reached the temperature of about 320° Centigrade, it is released by a second pressure-release valve to atmospheric pressure, whereby the remainder of the unsaponifiable constituents distils off with the steam. The remaining soap melt, which is at a temperature of 315° Centigrade, flows from the reaction chamber on to a cooling roller and is there obtained in the form of flakes. The flakes are ground and are suitable for the preparation of soap powders and other washing agents.

The pale-coloured crude soap may also be worked up into fatty acids. For this purpose the soap solution is acidified with 50 per cent. sulphuric acid and the crude fatty acids thus separated distilled with steam *in vacuo*. The following results are obtained:—

Distillation residue	Ester value of the fatty acids	Colour of the fatty acids in the 1 inch trough of the Lovibond Tintometer red
9 per cent.	0	0.3

There is thus obtained only a comparatively small distillation residue; the fatty acids obtained are free from esters and lactones and have a pale colour.

Dated this 12th day of November, 1936.
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PROVISIONAL SPECIFICATION
No. 25283 A.D. 1937.

Improvements in and Apparatus for removing the Unsaponifiable Constituents from Saponification Products of Oxidation Products of Non-aromatic Hydrocarbons of High Molecular Weight

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

The separation of unsaponifiable constituents from oxidation products of paraffin hydrocarbons, by evaporation of the unsaponifiable constituents frequently offers difficulties because in many cases undesirable side reactions, as for example decomposition of the soaps, take place.

My foreign correspondents have now found that the unsaponifiable constituents can be removed practically completely from such saponification products containing the same without injury to the soaps and in a very advantageous manner by spraying the saponification product which should contain water into a vaporising plant consisting of a tube system, by nozzles with the use of indifferent vapours or gases, particularly steam, the temperature of the products being so regulated, preferably while maintaining to a far-reaching extent the turbulent movement of the sprayed-in soap particles, that the soaps leave the vaporising plant in the liquid form. The vapours containing the unsaponifiable constituents thus produced may readily be separated from the soaps and are condensed as such.

Suitable initial materials for the process are saponification products of high molecular weight non-aromatic hydrocarbons, as for example hard or soft paraffin wax, middle oils, Deisel oils and non-aromatic hydrogenation products of coals, tars or oxides of carbon. They may be pretreated with advantage, before the saponification, with water, acids, dilute alkali solutions or organic solvents in order to remove readily soluble and strongly acid products. The saponification may be carried out with an amount of basic-acting agent which is calculated from the saponification value of the initial material, or with a larger amount, or preferably with a somewhat smaller amount. In the saponification solvents, as for example water or also organic solvents such as alcohols, ketones or hydrocarbons of higher boiling point, or mixtures of the said solvents may be used.

A larger or smaller amount of unsaponifiable constituents separates after the saponification depending on the nature of the oxidation product; these consist of high molecular weight alcohols, aldehydes, ketones, hydrocarbons and other neutral substances, and they separate as an upper layer. This layer is preferably separated before the further working up. The aqueous saponification product usually contains from about 25 to 60 per cent. of soaps and also still considerable amounts of unsaponifiable constituents in a dissolved or dispersed form. The spraying is carried out for example by heating the saponification product to high temperatures and then releasing it from pressure into the tube system. In this way the temperature is first reduced whereby at the same time the unsaponifiable constituents vaporise wholly or partly with the water. The soaps are led through the heated tube system in turbulent motion with the vapours in spray form. The most far-reaching possible maintenance of the turbulent motion of the sprayed-in soap particles is obtained by introducing the saponification product under comparatively high pressure into the tube system the tubes of which have a comparatively small diameter. By reason of the turbulent motion of the soap particles it is possible without detriment to heat the saponification product to high temperature, for example in many cases up to 400° Centigrade, and to use very short vaporisation periods and comparatively short vaporiser tubes. The tube system is heated by a heating device, as for example gas firing, and the temperature is regulated so that the sprayed soap liquefies and separates in the liquid form from the vapours in a separator and can be withdrawn.

It is not essential, however, to preheat the saponification product, for example in order to produce the pressure necessary for the spraying, but the spraying (or atomisation) of the saponification product containing more or less water can also be effected by nozzles with the use of water vapour, gases or the like.

It is of special advantage to subject the aqueous saponification product before introduction into the vaporisation plant, either alone or in admixture with solvents or diluents, to temperatures above 220°, preferably between about 250° and 330° Centigrade, whereby a considerable improvement in the saponification product is obtained. By the said heating, in particular, the over-oxidised acids present, as for example hydroxy-acids, lactones and the like, are converted into ordinary fatty acids and the yield of pure fatty acids is thus increased. This improvement is evident from the fact that the fatty acids obtained have no ester value or only a small ester value. The said pretreatment may also be carried out in the presence of agents having hydrogenating action, as for example while simultaneously pressing in hydrogen or with an addition of zinc dust or the like. The duration of the preheating of the saponification product is dependent on the nature of the saponification product; it is preferably carried on until a sample of the crude acids obtained from the saponification product no longer has an ester value.

It is advantageous to carry out the process according to this invention in a plant of the nature shown diagrammatically in the accompanying drawing, but the invention is not restricted to the particular plant shewn.

Referring to the drawing, 23 is a reservoir for the saponification product, 24 is a high pressure pump, 25 is a tube system in which if desired the preheating of the saponification product to temperatures above 220° Centigrade is effected, 26 and 27 are burners for heating the tube systems 25 and 30, 28 is a valve, 29 is a supply pipe for water vapour or the like provided with a valve, 30 is a tube system in which the spraying or atomisation of the saponification mixture takes place, 31 is an outlet for the heating gases, 32 is a syphon, 33 is a pipe through which the liquid soaps are withdrawn, 34 is a condensation device for the vapours containing the unsaponifiable constituents, 36 is a collecting vessel, 37 is a pipe provided with a valve for the withdrawal of the unsaponifiable constituents, 38 is a pipe provided with a valve for the withdrawal of the condensed water. Behind the pipe 38 there may be arranged a vacuum pump, as for example a steam jet aggregate, for the purpose of ensuring the fall in pressure to atmospheric in the tube system.

The following Examples, given with reference to the drawing, will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

2000 parts of an oxidation product having a saponification value of 107 (obtained by oxidation of hard paraffin wax with air at 115° Centigrade in the presence of 0.15 per cent. of potassium permanganate as catalyst) are saponified at 100° Centigrade with 412 parts of 35 per cent. caustic soda solution after the addition of 400 parts of water. After allowing the saponification product to stand for a short time, the major portion of the unsaponifiable constituents separates as an upper layer and is separated off. The saponification mixture is then introduced from the reservoir 23 by means of the pump 24 into the tube system 25 and heated therein to 330° Centigrade by the gas firing 26. After remaining for half an hour in the tube system 25 at 330° Centigrade and under a pressure of 130 atmospheres, the saponification mixture is released through the valve 28 into the tube system 30 to atmospheric pressure. Directly behind the pressure-release valve 28 there are simultaneously introduced through the valve 29 100 parts of steam at a temperature of 190° Centigrade per hour. The atomised saponification mixture and the steam are heated in the tube system 30 to about 350° Centigrade by means of the gas firing 27, whereby the unsaponifiable constituents still contained in the saponification product distil off with the steam. The soap melt then flows continuously through the separator 32 and the syphon 33 in an amount of about 30 parts per hour. The vaporous constituents are condensed in the condensation vessel 34 by trickling with water (introduced by the pipes 35) and collected in the collecting vessel 36. About 18 parts of unsaponifiable constituents per hour are withdrawn through the valve 37 and the condensed water flows through the outlet pipe 38.

The pale crude soap obtained in the said manner may be worked up into fatty acids with advantage. For this purpose the soap is dissolved in 50 per cent. of water and the solution is acidified with dilute sulphuric acid. The crude fatty acids thus separated are distilled *in vacuo* with steam. An acid having the following characteristics is thus obtained:—

Distillation residue	Ester value	Distilled fatty acid Colour in Lovibond tintometer (6" trough) red	Unsaponifiable constituents
10 per cent.	0	1	0.5 per cent.

If an oxidation product be used which has been oxidised at 90° Centigrade, the abovementioned half an hour period during which the product remains in the tube system 3 at 330° Centigrade can be dispensed with without the quality of the fatty acids being appreciably reduced.

Dated this 17th day of September, 1937.
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Agents.

COMPLETE SPECIFICATION

Improvements in and Apparatus for removing the Unsaponifiable Constituents from Saponification Products of Oxidation Products of Non-Aromatic Hydrocarbons of High Molecular Weight

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The separation of unsaponifiable constituents from saponification products containing the same, as for example saponification products of oils, fats, waxes or oxidation products of paraffin hydrocarbons, by evaporation of the unsaponifiable constituents frequently offers difficulties because in many cases undesirable side reactions, as for example decomposition of the soaps, take place. Moreover, in the preparation of soaps from the said oxidation products of non-aromatic hydrocarbons of high molecular weight (as for example paraffin wax), it is necessary that the saponification products should be substantially free from hydroxy fatty acids, lactones and the like as well as from polymeric constituents because these substances impart to the soaps an unpleasant odour and cause undesirable discolouration so that they are unsuitable for many purposes, as for example for domestic use.

My foreign correspondents have now found that the unsaponifiable constituents can be removed practically completely from saponification products of oxidation products from non-aromatic hydrocarbons of high molecular weight containing the same without injury to the soaps and in a very advantageous manner by introducing such a saponification product containing at least 25 per cent. of water under a pressure of about 100 atmospheres or more into a vaporising plant consisting of a tube system and releasing the pressure to atmospheric pressure within the tube system before the saponification product leaves it, the temperature in this tube system being so regulated that the soaps are always in the liquid form and are even heated within the tube system after the pressure has been released to atmospheric pressure so that they leave the vaporising plant in the liquid form and practically free from unsaponifiable constituents, while the latter are drawn off together with steam.

The initial materials for the process are saponification products of oxidation products of high molecular weight non-aromatic hydrocarbons, as for example hard or soft paraffin wax, paraffin oil, middle oils, Diesel oils, petroleum and non-aromatic hydrogenation products of coals, tars or oxides of carbon. They may be treated with advantage, before the saponification, with water, acids, dilute alkali solutions or organic solvents in order to remove readily soluble and strongly acid products. The saponification may be carried out with an amount of basic-acting agents which is calculated from the saponification value of the initial material, or with a larger amount, or preferably with a somewhat smaller amount. In the saponification solvents, as for example water or also organic solvents such as alcohols, ketones or hydrocarbons of higher boiling point, or mixtures of the said solvents, may be used.

Generally a larger or smaller amount of unsaponifiable constituents separates after the saponification depending on the nature of the oxidation product; these consist of high molecular weight alcohols, aldehydes, ketones, hydrocarbons and other neutral substances, and they separate as an upper layer. This layer is preferably separated before the further working up. The aqueous saponification product usually contains from about 25 to 60 per cent. of soaps and also still considerable amounts of unsaponifiable constituents in a dissolved or dispersed form. It is particularly advantageous to heat the saponified oxidation products together with at least an equal amount by weight of water calculated on the anhydrous crude saponified product.

The introduction of the water-containing saponification product into the heated vaporising plant may be effected by preheating the saponification product in a closed vessel thus producing the pressure necessary; but the introduction of the saponification products may also be effected by nozzles with the use of indifferent gases or vapours, particularly of steam. The duration of the treatment depends in general on the nature of the oxidation products, for example on their content of hydroxy fatty acids, lactones and the like. Frequently it is necessary to carry on the heat treatment for at least an hour. The most favourable temperatures for the process according to this invention lie between 310° and 350° Centigrade and it is advantageous to work at about 320° Centigrade. Under the said working conditions, a greatly increased pressure is usually set up; generally speaking it amounts to about 100 atmospheres or more.

The pressure of the heated saponification mixture is then released while further heating the mixture, whereby the unsaponifiable constituents are removed with the steam. The release of pressure is advantageously effected in stages, by which means it is ensured that the soap remains as long as possible in aqueous solution and sufficient steam is present for the removal of the whole of the unsaponifiable constituents. It is preferable first to release the pressure, by suitable regulation of valves, to a pressure of from 20 to 50 atmospheres; in this case, however, the temperature of the saponification product which is lowered by the release of pressure must be raised again to from 320° to 330° Centigrade or up to 380° Centigrade. Heating to the said temperature is also necessary for maintaining the soap in liquid state while further releasing the pressure to atmospheric pressure.

The process is preferably carried out continuously and the accompanying drawing (see Figure 1) illustrates an example of apparatus suitable for continuous operation; the invention is, however, not restricted to the particular example of apparatus shewn.

Figure 1 represents a diagrammatic view of a vertical section of a plant which may be employed for carrying out the process set forth above. 1 is a measuring vessel for the oxidation product, 2 is a measuring vessel for the caustic soda solution, 3 is a vessel with a stirrer 4 and a drain pipe 5 for the unsaponifiable material, 6 is a filter, 7 is a high-pressure pump, 8 is a check valve, 9 a tube system, 10 and 11 are pressure-release valves, 12 an inlet for the heating gases, 13 an outlet pipe for the waste gases, 14 a collecting vessel for the fused soap, 15 a cooling roller, 16 a cooler for the unsaponifiable constituents and steam, 17 a separating vessel for the unsaponifiable constituents, 18 a drain pipe for the condensed water, 19 a drain pipe for the unsaponifiable constituents and 20, 21 and 22 are manometers.

A special modification of this invention consists in spraying the saponification product containing at least 25 per cent. of water at elevated pressure into the heated vaporising plant.

The spraying is carried out for example by heating the saponification product to high temperatures and then releasing it from pressure into the tube system. In this way the temperature is first reduced whereby at the same time the unsaponifiable constituents vaporise wholly or partly with the water. The soaps are led through the heated tube system in turbulent motion with the vapours in sprayed form. The most far-reaching possible maintenance of the turbulent motion of the sprayed-in soap particles is obtained by introducing the saponification product under a high pressure into the tube system the tubes of which have a comparatively small diameter as is usual in pipe stills, for example about 30 millimetres. Generally speaking, the pressure to be used is dependent on the temperature of the heated water-containing saponification mixture. Pressures from 100 and 130 atmospheres are especially suitable.

By reason of the turbulent motion of the soap particles it is possible without detriment to heat the saponification product to high temperature, for example in many cases up to 400° Centigrade, and to use very short vaporisation periods and comparatively short vaporiser tubes for example of 30 metres length. The tube system is heated by a heating device, as for example gas firing, and the temperature is regulated so that the sprayed soap liquefies and separates in the liquid form from the vapours in a separator and can be withdrawn.

It is not essential, however, to preheat the saponification product, for example in order to produce the pressure necessary for the spraying, but the spraying (or atomisation) of the saponification product containing essential amounts of water can also be effected by nozzles with the use of water vapour, gases or the like.

It is of special advantage to subject the aqueous saponification product before introduction into the vaporisation plant, either alone or in admixture with solvents or diluents, for some time to temperatures above 220°, preferably between about 250° and 330° Centigrade, whereby a considerable improvement in the saponification product is obtained. By the said heating, in particular, the over-oxidised acids present, as for example hydroxy acids, lactones and the like, are converted into ordinary fatty acids and the yield of pure fatty acids is thus increased. This improvement is evident from the fact that the fatty acids obtained have no ester value or only a small ester value. The said pretreatment may also be carried out in the presence of agents having hydrogenating action, as for example while simultaneously pressing in hydrogen or with an addition of zinc dust or the like. The duration of the preheating of the saponification product is dependent on the nature of the saponification product; it is preferably carried on until a sample of the crude acids obtained from the saponification product no longer has an ester value.

When introducing the saponification products into the tube system while spraying it is advantageous to carry out the process according to this invention in a plant of the nature shewn in Figure 2 of the accompanying drawing which is a diagrammatic view of a vertical section of the plant. The invention, however, is not restricted to the particular plant shewn.

Referring to Figure 2, 23 is a reservoir for the saponification product, 24 is a high pressure pump, 25 is a tube system in which if desired the preheating of the saponification product to temperatures above 220° Centigrade is effected, 26 and 27 are burners for heating the tube systems 25 and 30. 28 is a valve, 29 is a supply pipe for water, vapours or the like provided with a valve, 30 is a tube system in which the spraying or atomisation of the saponification mixture takes place, 31 is an outlet for the heating gases, 32 is a syphon, 33 is a pipe through which the liquid soaps are withdrawn, 34 is a condensation device for the vapours containing the unsaponifiable constituents, with two water supplying pipes 35, 36 is a collecting vessel, 37 is a pipe provided with a valve for the withdrawal of the unsaponifiable constituents, 38 is a pipe provided with a valve for the withdrawal of the condensed water. Behind the pipe 38 there may be arranged a vacuum pump, as for example a steam jet aggregate, for the purpose of ensuring the fall in pressure to atmospheric in the tube system.

The following Examples, given with reference to the drawings, will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

A product obtained by the oxidation of hard paraffin wax in the liquid phase by leading in air at 150° Centigrade with an addition of manganese naphthenate as catalyst, is intimately mixed with a 20 per cent. solution of caustic soda, at 90° Centigrade in the stirring vessel 3 (see Figure 1) in an amount containing 4 per cent. of caustic soda less than corresponds to the amount theoretically necessary for the complete saponification of the fatty acids and esters. Water is added to the saponification mixture in such an amount that in all the final mixture contains 70 per cent. of water. The unsaponifiable constituents separate as the top layer on standing; they are withdrawn through the drain pipe 5 after the lower layer has left the stirring vessel at its bottom and before new oxidation product is introduced into this vessel. The soap solution is pumped through the filter 6 with the aid of the high-pressure pump 7 and through the check valve 8 into the tube system 9 and heated therein to from 310° to 320° Centigrade; the speed of flow is regulated so that a pressure of 160 atmospheres is set up and the saponification mixture remains in the tube system for about 2 hours. The uniform maintenance of the pressure is regulated by the release valve 10. The pressure is then released in stages, the first stage being by means of the valve 10 from 160 to 25 atmospheres. With the effluent vapours a part of the unsaponifiable material is removed from the saponification mixture. The saponification mixture is then released to atmospheric pressure by a second valve 11, whereby the unsaponifiable constituents as well as coloured constituents and odorous substances are practically completely removed with the steam.

The remaining soap melt is pale in colour. It is led into the collecting vessel 14 and passes thence to a cooling roller 15 on which it is worked up into flakes. The steam with the unsaponifiable constituents passes through the collecting vessel 14 into the cooler 16 in which the condensation takes place. The unsaponifiable constituents are collected in the separation vessel 17 and supplied to the oxidation again through the drain pipe 19. The condensed water may be removed through the drain pipe 18.

The crude soap obtained is dissolved in water and then acidified with dilute sulphuric acid. The crude acids thus separated, which contain only from 0.5 to 1 per cent. of unsaponifiable constituents, are distilled with steam under a pressure of 2 millimetres (mercury gauge). The following results are thus obtained:—

Distillation residue	Ester value of the fatty acids	Colour of the fatty acids in the 1 inch trough of the Lovibond Tintometer red
18 per cent.	0	1.0

The fatty acids obtained are free from lactones, hydroxy acids and the like and have a very pale colour.

Example 2.

400 parts of an oxidation product having a saponification value of 146 (obtained by the oxidation of hard paraffin wax with air at 115° Centigrade with an addition of sodium palmitate as catalyst) are saponified after the addition of 200 parts of water and 116 parts of 35 per cent. caustic soda solution. After allowing to stand for a short time, a part of the unsaponifiable constituents separates on the surface of the same and is removed, the saponification mixture then being introduced into the tube system shewn in Figure 1 and heated to 315° Centigrade. After treatment for 1½ hours under a pressure of 150 atmospheres, the saponification mixture is released to a pressure of 80 atmospheres, the major portion of the unsaponifiable constituents being removed with the effluent steam. As soon as the saponification mixture has again reached the temperature of about 320° Centigrade, it is released by a second pressure-release valve to atmospheric pressure, whereby the remainder of the unsaponifiable constituents distils off with the steam. The remaining soap melt, which is at a temperature of 315° Centigrade flows from the reaction chamber on to a cooling roller and is there obtained in the form of flakes. The flakes are ground and are suitable for the preparation of soap powders and other washing agents.

The pale-coloured crude soap may also be worked up into fatty acids. For this purpose the soap solution is acidified with 50 per cent. sulphuric acid and the crude fatty acids thus separated distilled with steam in vacuo. The following results are obtained.

Distillation residue	Ester value of the fatty acids	Colour of the fatty acids in the 1 inch trough of the Lovibond Tintometer red
9 per cent.	0	0.3

There is thus obtained only a comparatively small distillation residue; the fatty acids obtained are free from esters and lactones and have a pale colour.

EXAMPLE 3.

2000 parts of an oxidation product having a saponification value of 107 (obtained by oxidation of hard paraffin wax with air at 115° Centigrade in the presence of 0.15 per cent. of potassium permanganate as catalyst) are saponified at 100° Centigrade with 412 parts of 35 per cent. caustic soda solution after the addition of 400 parts of water. After allowing the saponification product to stand for a short time, the major portion of the unsaponifiable constituents separates as an upper layer and is separated off. The saponification mixture is then introduced from the reservoir 23 (see Figure 2) by means of the pump 24 into the tube system 25 and heated therein to 330° Centigrade by the gas firing 26. After remaining for half an hour in the tube system 25 at 330° Centigrade and under a pressure of 130 atmospheres, the saponification mixture is released through the valve 28 into the tube system 30 to atmospheric pressure. Directly behind the pressure-release valve 28 there are simultaneously introduced through the valve 29 100 parts of steam per hour at a temperature of 190° Centigrade. The atomised saponification mixture and the steam are heated in the tube system 30 to about 350° Centigrade by means of the gas firing 27, whereby the unsaponifiable constituents still contained in the saponification product distil off with the steam. The soap melt then flows continuously through the separator 32 and the syphon 33 in an amount of about 30 parts per hour. The vaporous constituents are condensed in the condensation vessel 34 by trickling with water (introduced by the pipes 35) and collected in the collecting vessel 36. About 13 parts of unsaponifiable constituents per hour are withdrawn through the pipe 37 and the condensed water flows through the outlet pipe 38.

The pale crude soap obtained in the said manner may be worked up into fatty acids with advantage. For this purpose the soap is dissolved in 50 per cent. of water and the solution is acidified with dilute sulphuric acid. The crude fatty acids thus separated are distilled in vacuo with steam. An acid having the following characteristics is thus obtained:—

Crude acid	Distilled fatty acid		
Distillation residue	ester value	Colour in Lovibond Tintometer (6 inch trough) red	Unsaponifiable constituents
10 per cent.	0	I	0.5 per cent.

If an oxidation product be used which has been oxidised at 90° Centigrade, the above-mentioned half an hour period during which the product remains in the tube system 25 at 330° Centigrade can be dispensed with without the quality of the fatty acids being appreciably reduced.

I am aware that it has been proposed to remove unsaponifiable constituents from saponification products of oxidation products from non-aromatic hydrocarbons of high molecular weight by passing the water-containing saponification products into a vaporising plant consisting of a tube system (1) at high pressure, for example 50 to 150 atmospheres and releasing the pressure to atmospheric at the end of the tube, or (2) at pressures from 18 to 30 atmospheres and releasing the pressure to atmospheric within the tube system.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for removing the ununsaponifiable constituents from saponification products of oxidation products from non-aromatic hydrocarbons of high molecular weight containing the same,

which comprises introducing such a saponification product containing at least 25 per cent. of water under a pressure of about 100 atmospheres or more into a vaporising plant consisting of a tube system and releasing the pressure to atmospheric pressure within the tube system before the saponification product leaves it, the temperature in the tube system being so regulated that the soap is always in the liquid form and is even heated within the tube system after the pressure has been released to atmospheric pressure so that it leaves the vaporising plant in the liquid form and practically free from unsaponifiable constituents, while the latter are withdrawn together with steam.

2. In the process as claimed in claim 1, preheating the water-containing saponification product to a temperature above 220° Centigrade.

3. In the process as claimed in claim 1 or 2, introducing the water-containing saponification product into the vaporising plant while simultaneously leading in indifferent vapours or gases.

4. In the process as claimed in any of claims 1 to 3, releasing the pressure to atmospheric pressure in stages.

5. A process as claimed in any of claims 1 to 4, which comprises spraying the water-containing saponification product into the vaporising plant consisting of a tube system and releasing the pressure to atmospheric pressure within the tube system before the saponification product leaves it while maintaining to a far-reaching extent the turbulent movement of the sprayed-in soap particles by introducing the saponification product under a sufficiently high pressure.

6. In the process as claimed in any of claims 1 to 5, employing saponification products containing at least an equal amount of water.

7. The process for removing the unsaponifiable constituents from saponification products of oxidation products from non-aromatic hydrocarbons of high molecular weight containing the same substantially as described in each of the foregoing Examples.

8. Purified saponification products when obtained according to the process particularly described and ascertained.

9. The use for carrying out the process of any of claims 1 to 7 of apparatus for removing unsaponifiable constituents from saponification products of oxidation products from non-aromatic hydrocarbons of high molecular weight containing the same constructed and adapted to be operated substantially as herein described or shewn in the accompanying drawings.

Dated this 27th day of October, 1937.

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Agents.

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487,317 PROVISIONAL SPECIFICATION Nº 30,937/36 *1 SHEET*

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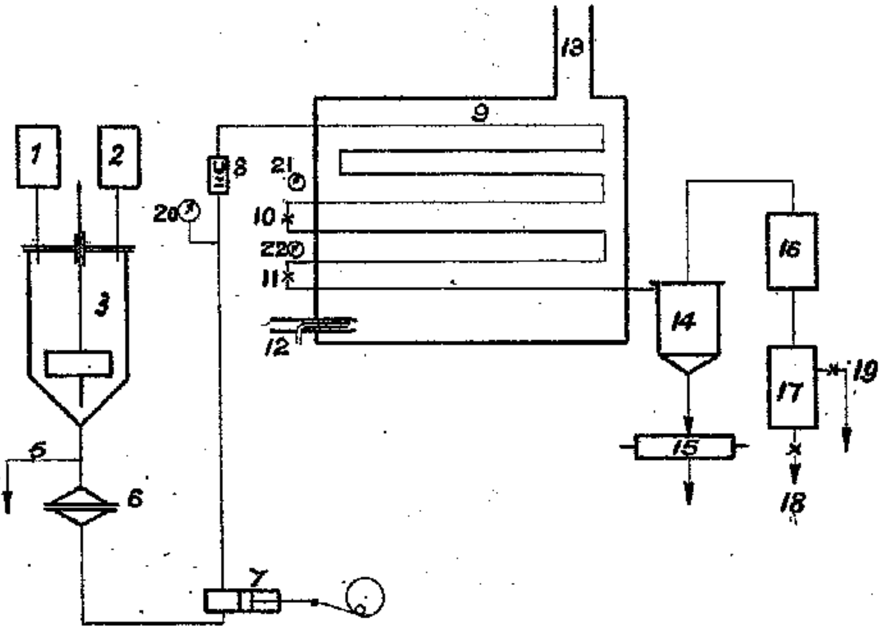

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487,317. PROVISIONAL SPECIFICATION Nº 25,283^{37} 1 SHEET

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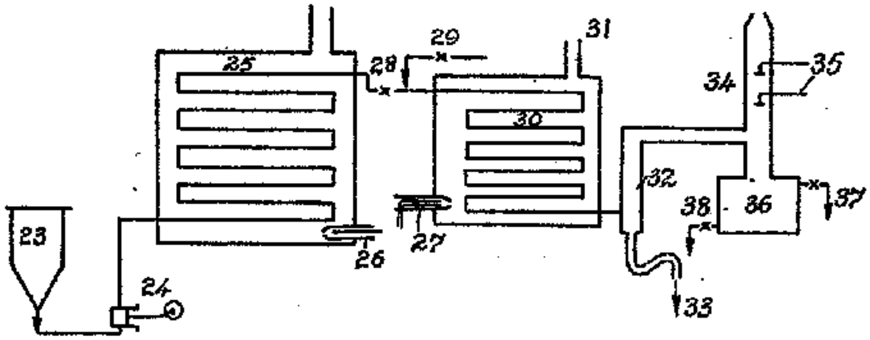

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487,317 COMPLETE SPECIFICATION 1 SHEET

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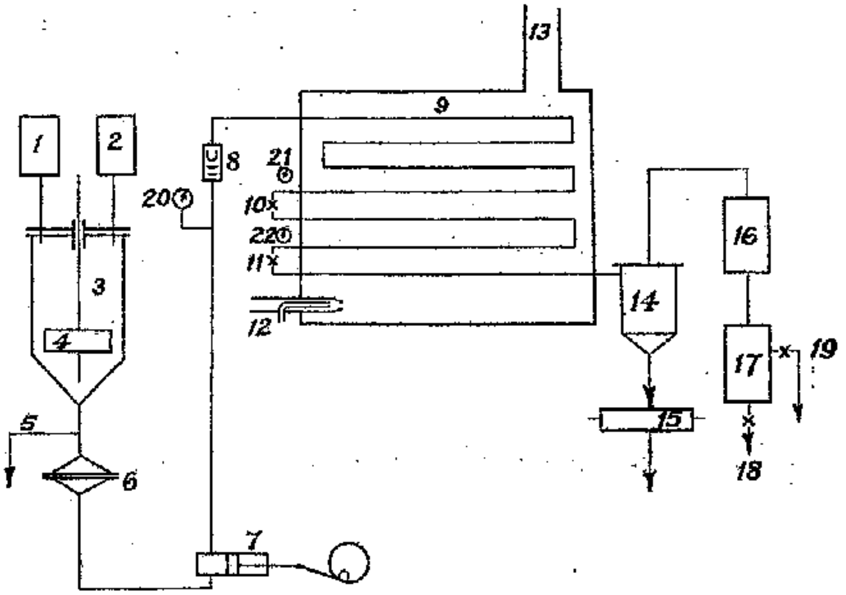

Fig. 1.

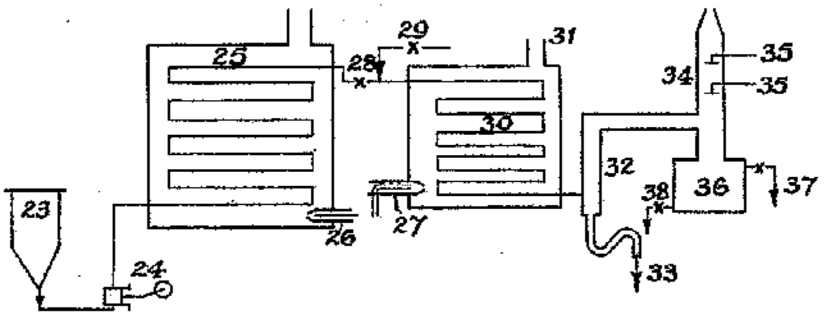

Fig. 2.

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