

[54] **METHOD FOR THE REMOVAL OF NON-SATURATED AND/OR AROMATIC HYDROCARBONS FROM SATURATED PARAFFIN HYDROCARBONS AND A DEVICE TO EMBODY SAID METHOD**

[75] Inventor: **Alfred Davidsohn**, Locarno, Switzerland

[73] Assignee: **Ballestra S.p.A.**, Milan, Italy

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Primary Examiner—Delbert E. Gantz
Assistant Examiner—Juanita M. Nelson
Attorney, Agent, or Firm—Robert E. Burns;
Emmanuel J. Lobato; Bruce L. Adams

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[58] Field of Search 208/293, 273, 268

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[57] ABSTRACT

The invention generally aims at removing completely non-saturated and/or aromatic hydrocarbons or other sulphonatable compounds from saturated paraffin hydrocarbons and particularly at producing white oils from portions of crude oil with a high distillation range, containing relatively large quantities of sulphonatable aromatic compounds.

9 Claims, 6 Drawing Figures

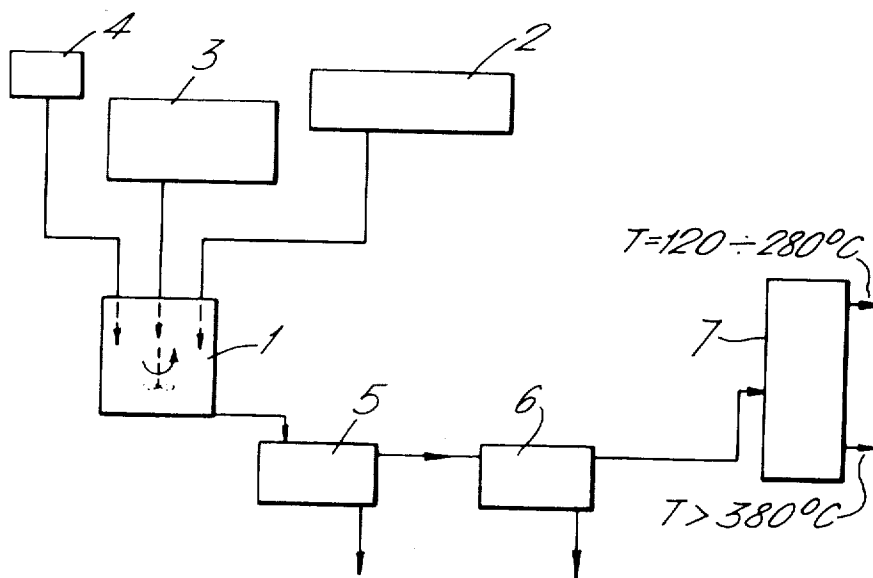
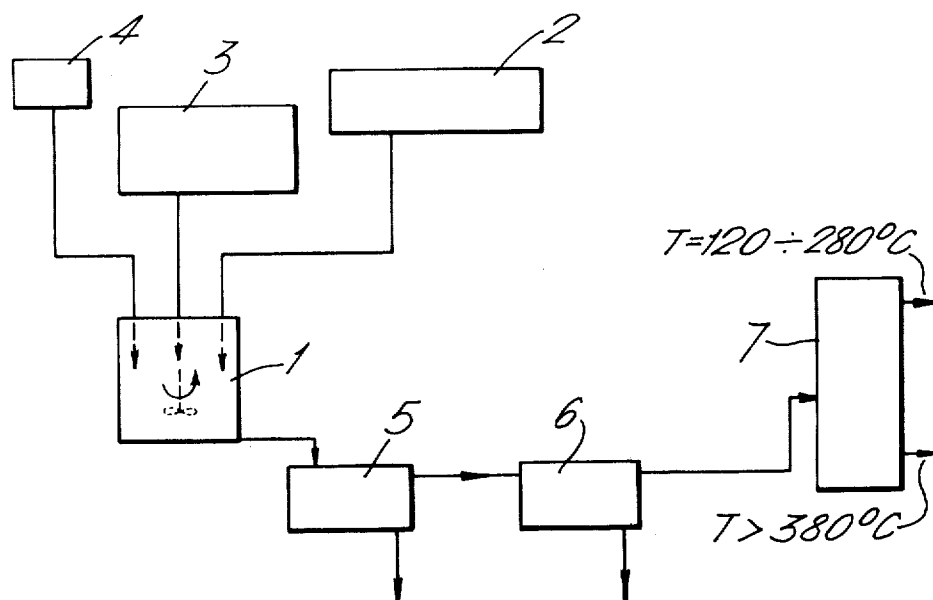


Fig. 1.



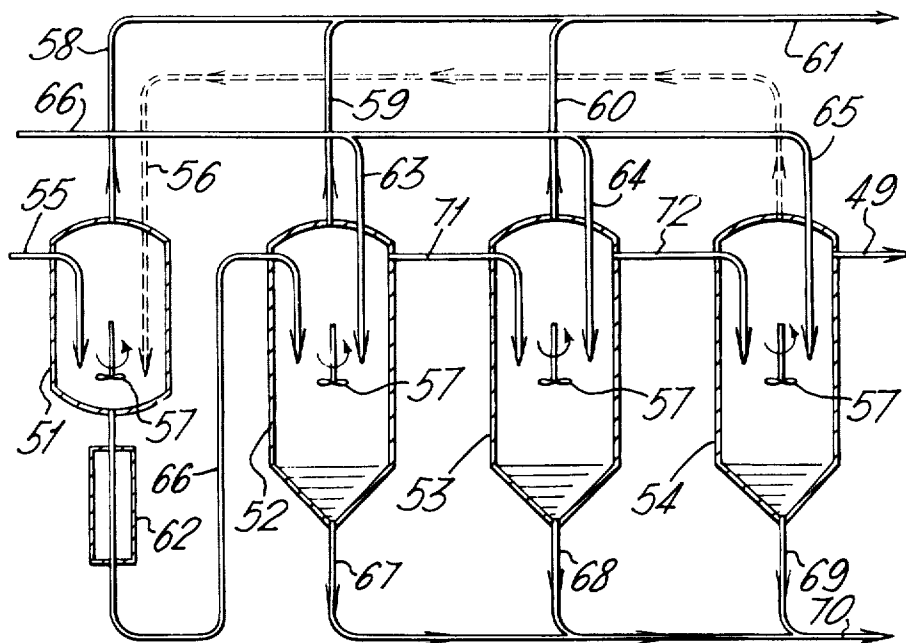


Fig. 2.

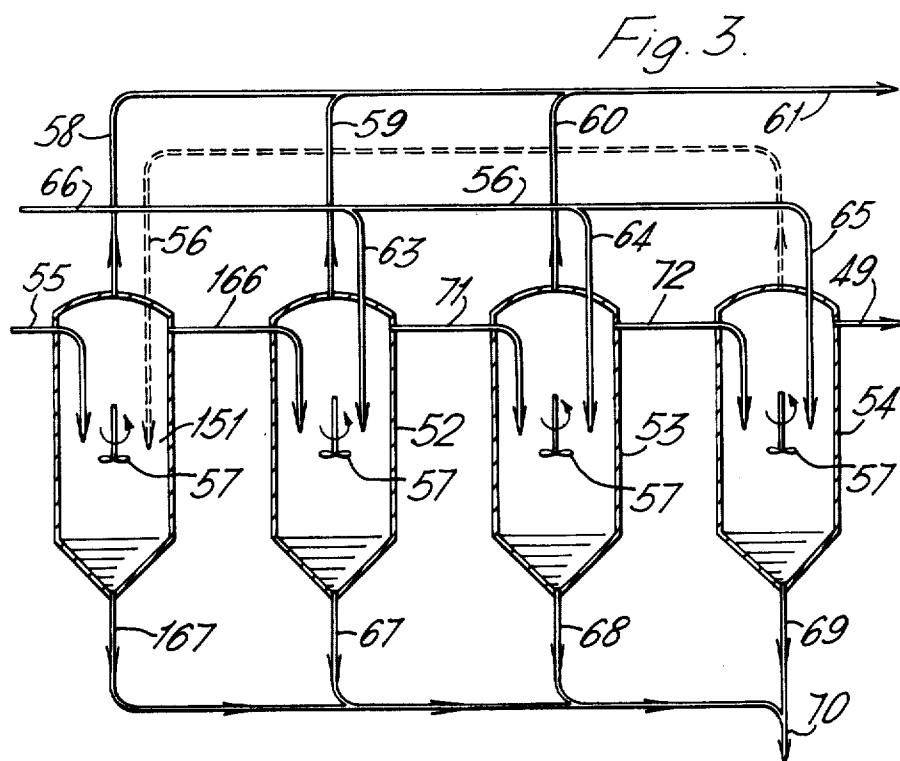


Fig. 3.

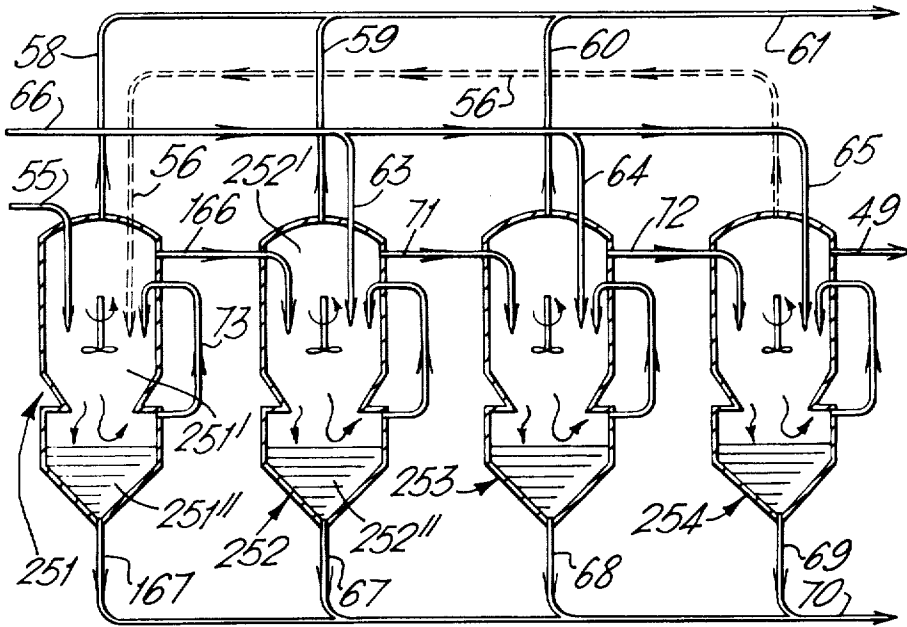


Fig. 4.

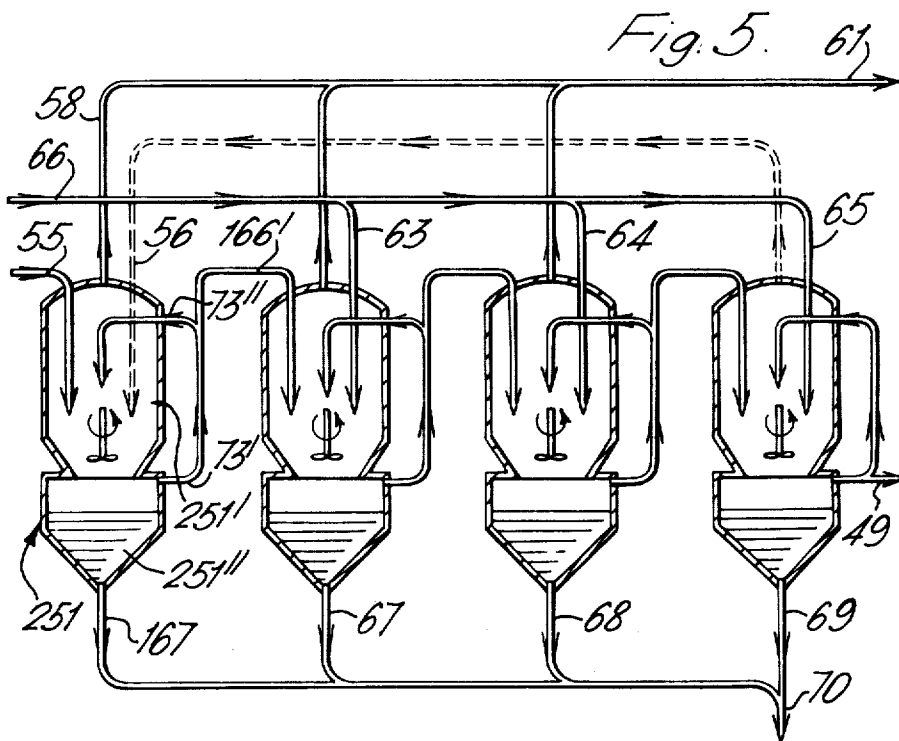
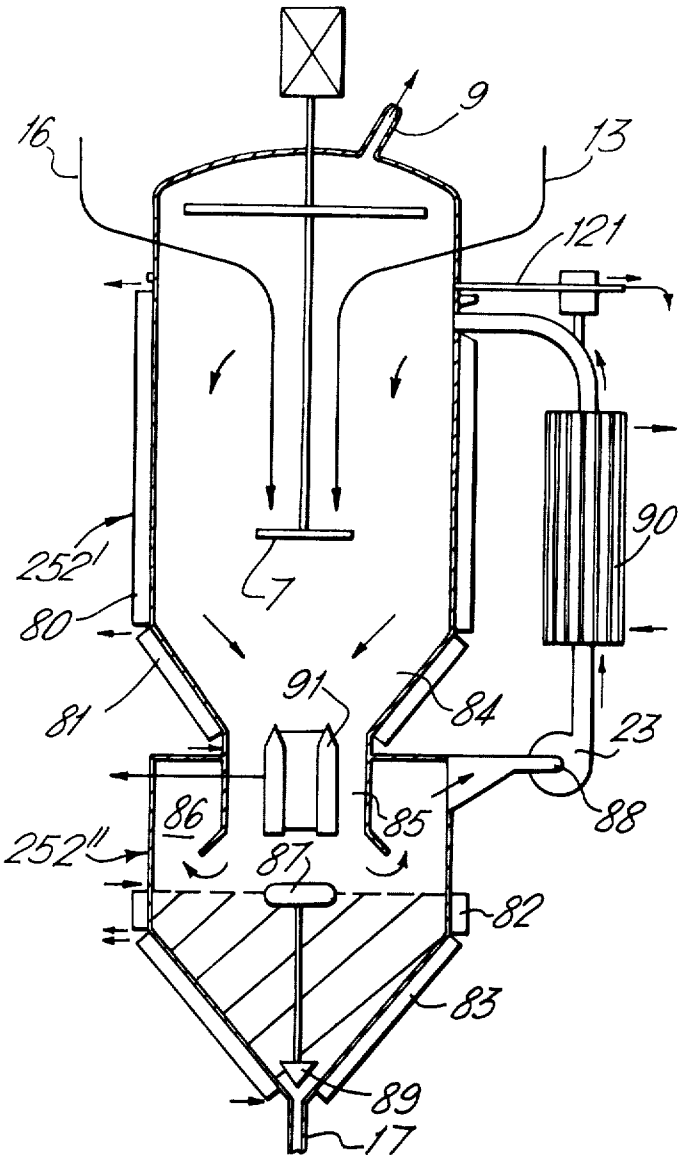


Fig. 5.

Fig. 6.



METHOD FOR THE REMOVAL OF NON-SATURATED AND/OR AROMATIC HYDROCARBONS FROM SATURATED PARAFFIN HYDROCARBONS AND A DEVICE TO EMBODY SAID METHOD

BACKGROUND OF THE INVENTION

The present invention relates generally to a method and device for the complete removal of non-saturated or/and aromatic hydrocarbons or other sulphonatable compounds from saturated paraffin hydrocarbons and particularly to a method and device for producing white oils from portions of crude oil with a high distillation point, containing relatively large quantities of sulphonatable aromatic compounds.

White oils are a particular type of highly refined mineral oils containing only paraffin hydrocarbons and isoparaffins (naphthenics). They are used for various purposes, when the absence of colour, taste and smell is absolutely required. Various types of white oils are produced and, correspondingly to the use they are intended for, they differ from one another according to the degree of refining and their viscosity. The raw material for obtaining said white oils consists of various types of hydrocarbons (paraffinic, naphthenic, aromatic) and small quantities of organic compounds containing sulphur, oxygen and nitrogen.

The aromatic hydrocarbons (mono-, di-, policondensate) with shorter or longer paraffinic side-chains, branched or straight, and organic compounds containing sulphur, oxygen and nitrogen, are responsible for color, taste, smell and irritation of the human skin, and are to be removed during the refining process.

Generally, in the process on an industrial scale, a sulphonation process is used for removing said undesirable compounds.

First, Oleum was used, with various percentages of free SO_3 , as sulphonating agent, however, by said sulphonating agent a large amount of insoluble sulphonic acids in the form of sludge is obtained. These acids retain a good deal of oil-soluble sulphonated compounds which could be used as by-products, whereas said sludges cannot be used as by-products.

Further, sulphonation with Oleum is a reaction wherein the sulphonating agent is used in large excess, whereby a considerable part of the mono-sulphonic acids soluble in oil, and thus usable as by-products, are degraded to insoluble polysulphonic acids which cannot be used at all as by-products.

The disadvantages caused by the sulphonation with Oleum was overcome by using, according to a method patented by the applicants, gaseous SO_3 derived directly from the combustion of proportioned amounts of molten sulphur and from the subsequent catalytic transformation of the produced SO_2 into SO_3 whose high reactivity is reduced by the fact that it is diluted in the carrier gas consisting of nitrogen, oxygen and small quantities of SO_2 .

However, even when gaseous SO_3 obtained as above is used as sulphonating agent, difficulties may arise in separating the non-sulphonated portion of oil and the sulphonic acids soluble in oil from the insoluble sludges consisting mainly of polysulphonic acids.

Particularly when the percentage of sulphonatable compounds is relatively high, e.g., higher than 20%, it is often very difficult, if not impossible to separate said acid sludges from the treated material. Not only the

separation through sedimentation difficult, but even centrifugation is very difficult or technically impossible (that is not practical on an industrial scale in an economically convenient manner). Particularly when said sludges are viscous and sticky, they tend to stick onto the walls of the reaction vessels, separation vessels or centrifuges.

The more difficult the separation, the higher the loss of the treated material. Furthermore, it is to be noted that the higher the viscosity, molecular weight and boiling point of the starting material, the higher the temperature during the sulphonating process.

Because of the higher temperatures secondary undesirable reactions, like polymerization, condensation and oxidation, and increases in the formation of disulphonates take place.

Said secondary reactions are largely responsible for the viscous nature of the formed acid sludges, the loss of valuable oil-soluble petro-sulphonates, and the formation of excessive amounts of sulphur trioxide which must be removed from the exhaust gases of the apparatus, so as to meet the more and more stringent laws against air pollution.

OBJECTS OF THE INVENTION

In view of the foregoing, the invention aims at achieving the following objects:

- to improve the separation of acid sludges;
- to lower the temperature of the sulphonation step in the process, thereby preventing excessive secondary reactions as well as the formation of SO_2 ;
- to increase the yield of refined material; and finally
- to improve the quality of oil-soluble sulphonated compounds.

Now, it is to be noted that recently the use of solvents of the so-called "Odorless" type, coming from petroleum, has considerably increased.

Such a type of solvent, based on portions of "Kerosene" type fractions with a distillation range between 120° and 280°C , is largely used in the production of aerosol products, for instance cosmetics, and as solvents for pesticides.

Though the above final products, as well as the starting material, are substantially different of the above white oils and of the oil portion from which said white oils are to be derived, this type of solvent too is obtained by sulphonating, e.g., through gaseous SO_3 , the non-paraffinic components, e.g., the aromatic or olefines compounds and other sulphonatable compounds, present in feedstock.

In these circumstances, this invention achieves the advantages shown in the above paragraphs 1 to 4 in producing white oils, starting with crude oils with a high content of sulphonatable compounds, by pre-mixing the starting material consisting of high molecular weight oil compounds with a starting material consisting of lower molecular weight fractions, the latter having also a lower viscosity and a lower distillation range.

It is convenient to use as low molecule weight starting material fractions consisting low molecular weight fractions of a type that when treated by sulphonation gives a commercially valuable product.

To this end fractions with a distillation temperature between 120° and 280°C may be used. Starting starting materials of high molecule weight consisting of high molecular weight oil fractions, i.e. oil compounds with

a distillation temperature above 320°C are used. It is to be noted that the temperature gap between the end point of the distillation range of the lower molecular weight fraction and the starting point of the distillation range of the higher molecular weight fraction is advantageous as it facilitates subsequently the separation of the refined products by distillation.

The low boiling point fractions, after the refining by the sulphonation method, are commercially valuable products commonly known as "Deodorized" solvents, or "Deodorized white spirits" and/or "Deodorized kerosene."

The effect of such pre-mixing is not only to change the character of the starting material, e.g., by decreasing the viscosity, lowering the reaction temperature, but also to change the character of the acid sludge.

The lower molecular weight sulphonatable compounds of the lower fraction have also a much lower viscosity, whereby the acid sludges of the mixture treated by sulphonation, become less viscous, more fluid, and retain less treated material.

The still slightly acid mixture is subject to the usual steps of neutralization, alkaline washing, and so on, the sulphonated compounds, soluble in oil, are thus removed by known methods, e.g., by a washing with hydroalcoholic solutions. The acid free mixture is then subjected to distillation, thereby separating the higher molecular weight material from the lower molecular weight material. As said above, it is at this point of the claimed process that the temperature gap between the upper end point of the distillation range of the lower molecular weight fraction and the starting point of the distillation range of the higher molecular weight fraction is particularly advantageous so as to effect such a separation without difficulty.

It is to be noted that by the process according to the invention, it becomes possible to use oleum for sulphonating sulphonatable compounds; though the use of gaseous SO_3 diluted in an inert carrier gas is preferable.

According to a variation of the present invention, its application range may be widely arranged as larger both for variation of the starting material, (feedstock) and for obtaining lowest amounts of aromatic compounds remaining in the refined products when said lowest limit is to be reduced to some dozens of parts per million.

It was said above that in order to reduce to the minimum the formation of insoluble poly-condensates, the sulphonation reaction of said compounds is effected by using a substantially limited quantity of SO_3 diluted in an inert carrier gas.

It has been found now that when it is desired to lower, in the final refined product, the percentage of non-sulphonated aromatic compounds to some dozens of parts per million, a stoichiometric amount of gaseous reagent cannot be used. It is necessary to use an excess, with the inconvenience that the process gives a lower yield with an increase of insoluble sludge and losses of oil-soluble sulphonates which are entrapped and lost in the said sludges.

Object of said variation of the invention is to avoid such an inconvenience, by ensuring a high degree of removals of the aromatic hydrocarbons from the refined end product.

The process according to the invention for obtaining purified saturated hydrocarbons, and particularly white oils, from fractions of high distillation point crude oil,

said portions containing large quantities of sulphonable aromatic compounds, is characterized in that said fractions of high distillation range crude oil are previously mixed with fractions of lower distillation crude oils also containing sulphonatable aromatic compounds. Said mixture is then subjected to sulphonation, separation of the sludges consisting of the oil insoluble sulphonic acids, neutralization and separation of the oil soluble sulphonic acids; finally the refined lower fraction is distilled off between 120° and 280°C leaving the higher fraction boiling above 320°C, so as to obtain first compounds known as deo-kerosene and then white oils.

The fraction of high distillation range crude oil may contain 35% by weight of sulphonable compounds. The fraction of low distillation range crude oil may contain sulphonable compounds up to 30% by weight.

According to the invention, the sulphonation of the mixture of crude oil fraction, the separation of the insoluble sludges, the neutralization, and the separation of the oils soluble sulphonic acids, are effected in several stages.

The starting fraction of the hydrocarbons with a high distillation range has the following characteristics:
average molecular weight between 315 and 400;
density between 0.865 and 0.890;
kinematic viscosity between 12 and 35 cts (At 100°F);

contents of sulphonable compounds up to 35% by weight;
boiling temperature higher than 320°C.

The starting of fraction of hydrocarbons with a low distillation point has the following characteristics;
boiling temperature between 120° and 280°C;
contents of sulphonable compounds up to 30% by weight.

According to a preferred embodiment of the invention, for separating the portion of aromatic compounds from the hydrocarbons mixture, said aromatic hydrocarbons are sulphonated in at least two stages in a series of reactors where the mixture is treated with the sulphonating agent fed into the reactors in parallel.

Such a method according to the invention is characterized in that the sulphonating agent is fed in parallel in decreasing portions at the stage subsequent to the first one, and the excess of sulphonating agent is removed from the last stage, is fed to the first one, so that said sulphonating agent is present in excess in the last reaction vessel, while the aggregate amount of sulphonating agent is used is about equal to the stoichiometric amount.

According to the invention, said sulphonating agent consists of gaseous SO_3 which is obtained by burning molten sulphur and then transforming the obtained SO_2 into SO_3 in presence of a catalyst. The gaseous reagent so obtained has the following volume composition:

$\text{SO}_3 = 6$ to 10.0%
 $\text{SO}_2 = 0.1$ " 0.2%
 $\text{N}_2 + \text{O}_2 = 93.9$ " 89.8%

Said gaseous sulphonating agent is fed into the liquid feedstock to be treated and dispersed therein by stirring so as to limit as much as possible polysulphonation of the aromatic components.

According to the invention, the feeding of said two reagents to each reaction step is accompanied by the removal of the insoluble compounds produced by the sulphonation of the aromatic portion, so that such a

portion, already sulphonated, cannot participate in the successive treatment of said liquid mix.

According to a particular embodiment of the invention, a portion of liquid compounds treated in each stage, after the separation of the insoluble portion, is partly recycled so as to dilute both the sulphonable portion of the liquid compound to be treated and the gaseous reagent which is dispersed within the liquid mass of the compound to be treated.

The device for embodying the process according to the invention comprises a set of reaction vessels in series for the passage between each other of the liquid mix to be treated, feeding in parallel the gaseous reagent, as well as removing, by separating devices, the insoluble compounds obtained by the reaction in each individual reaction vessel, removing devices for the unreacted gaseous portions from the corresponding reaction vessel, said devices for removing the gaseous reaction from the last reaction vessel are connected to the feeding device of said gaseous reagent to the first reaction vessel.

The device according to the invention further comprises agitators for dispersing said gaseous reagent within the mix of liquid feedstock to be treated and thermoregulators suitable to ensure the desired temperature in the various zones of each reaction vessel.

The device according to the invention is finally characterized in that in one embodiment, each reaction vessel is divided into two overlapped elements both formed by an upper cylindric zone joined at its bottom to a conical or frusto-conical zone; wherein said upper element penetrates the lower one by a cylindric projection so as to originate in the upper zone of the lower element an annular section for collecting the liquid reaction mixture; a suitable baffle being arranged at the opening of said cylindric projection of the upper element, so as to prevent the fluid current coming from the upper element from removing the layer of insoluble compounds of the reaction deposited on the bottom of said lower element.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be clearly understood, it will be now described, by way of example only, with reference to the accompanying drawings, wherein:

FIG. 1 shows a general flow diagram of the process according to the invention;

FIG. 2 shows in greater details the part of the apparatus wherein the sulphonation of the unsaturated hydrocarbons, according to a first variation of embodiment, is effected;

FIGS. 3, 4 and 5 are similar to FIG. 2, but refer to three further variations of the apparatus for embodying the invention;

FIG. 6 shows in enlarged scale one of the reaction vessels shown in FIG. 4 above.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

With particular reference to FIG. 1, the sulphonation device 1 receives jointly from 2 the heavy portion of crude oil from which the pure paraffinic compounds are to be derived, from 3 the portion of crude oil from which the so-called deo-kerosene is to be derived, and finally from 4 the gaseous SO_3 diluted in a carrier gas consisting mainly of nitrogen, oxygen and smaller portions of SO_2 . It is to be noted that numeral 4 does not

denote a stock of SO_3 , but a device for the proportioned product ion thereof.

The apparatus for producing proportionally SO_3 comprises, as above said, a proportioning means of molten sulphur, a combustion means for same for producing SO_2 and finally a catalyst chamber (converter) for transforming SO_2 into SO_3 . The percent of SO_3 in the gas coming from 4 is between 5 and 12%, preferably about 7%, which value corresponds to the contents of SO_3 normally obtained when molten sulphur is burned and converted to SO_3 . Similarly, the molten sulphur, and thus indirectly SO_3 coming from 4, is proportioned, so as to provide said SO_3 in a quantity relating to the molecular weight and the average contents of sulphonable compounds in feed stocks.

The reaction vessel 1 is provided with stirring and thermoregulating devices, generally consisting of suitably selected refrigerating systems, such as cooling coils and the like.

It is to be noted that the liquid mix coming from 1 contains insoluble polysulphonic acids, which are separated in 5, oil soluble monosulphonic acids, which are neutralized and then separated in 6, as well as paraffinic compounds which were not sulphonated and are conveyed to the distillation tower. In said distillation tower, at a distillation temperature of 120° to 280°C the so-called deo-kerosene distills, while the white oil which distills at a considerably higher temperature, above 320°C , and remains as bottom.

It is further to be noted that the sulphonation may be divided into more reaction steps in series, each of them formed in sequence by a reaction vessel receiving SO_3 in parallel, by a separator for the insoluble sludges, by a neutralizer-separator for the oil soluble sulphonic acids.

The flow diagram shown in FIG. 1 will be better understood with the reference to the following examples. Example No. 1

160 kgs of a starting material for producing white oils, with an average molecular weight of 320 and containing sulphonable compound in an amount up to 25% by weight and with a distillation range starting from 320°C , were mixed with 40 kgs of kerosene with a distillation range between 140° and 260°C and containing sulphonable compounds in an amount up to 25% by weight.

Said mix is treated at a temperature between 35° and 40°C with 27 kgs of gaseous SO_3 mixed with a carrier gas in a percent of 7%; such a gaseous mixture contains SO_3 coming directly from a combustion for producing SO_3 from molten sulphur. After said reaction, the materials participating therein are left depositing: 61 kgs of green acids are thus obtained, which are to be disposed by burning. Furthermore, are obtained 164 kgs of "Acid oil" which is subjected to washing with a hydroalcoholic solution of sodium hydroxide. In the alcohol 14 kgs of sulphonated products, soluble in oil, are obtained. Further 151 kgs of a mix free of acids are obtained, which then undergo distillation. From said mix 29 kgs of refined kerosene, are obtained by distillation at temperatures from 140° to 260°C , with a bottom of 110 kgs of refined white oils. The portion of white oils and kerosene may be treated with 1% of decolorizing Fullers earth so as to obtain absolutely colorless products.

Example No. 2

150 kgs of a starting material for producing white oils, with an average molecular weight of 370, containing sulphonable compounds in an amount of 30% by weight and with a distillation range starting from 350°C, were mixed with 50 kgs of kerosene, with a distillation range between 140° and 280°C, and containing 25% of sulphonable compounds. Said mix was treated with 28 kgs of gaseous SO₃ diluted into a percentage of 7% in a carrier gas and coming directly from an apparatus for producing SO₃ from molten sulphur. The sulphonation reaction was effected at a temperature between 35° and 45°C. When the reaction was over the mix was left to deposit. The products obtained were: 67 kgs of green acids and 160 kgs of acid oils which were washed with a hydroalcoholic solution of sodium hydrate, so as to give 15 kgs of oil-soluble sulphonated compounds and 145 kgs of a refined mix free of acids and consisting of deodorized kerosene and white oils.

Said mixture was finally subjected to distillation between 140° and 280°C, yielding 37 kgs of refined kerosene and a residue of 103 kgs of refined white oils. Both said portions were subjected to decoloration with decolorizing earth.

Reference will be made now to FIGS. 2 to 6 concerning said part of the device according to the invention where the sulphonation of the unsaturated compounds is accomplished. It is to be appreciated that said FIGS. show preferred variations of apparatus utilization in one of the steps of the claimed process. At the same time, it may not be excluded that said process could be used for sulphonating sulphonatable compounds where the main reaction product consists of sulphonic acids, or for removing the sulphonable compounds through sulphonation from raw materials different in proportion from the ones above mentioned and to which the process of this invention is particularly directed.

With reference to FIG. 2, the device according to the invention comprises a set of four reaction vessels 51, 52, 53 and 54, and first of which has also and primarily the task of pre-mixing the mixture of reagents.

A stirring device, e.g. of a helical nature, 57 is provided in the core of each reactor, that is at a given distance from the bottom thereof, for the reasons mentioned herebelow.

The liquid mix to be treated is introduced to close said stirring means 57 in the reactor-mixer 51, through 55. The exhaust gases caused by the reaction and collecting in the upper part of reaction vessels 51, 52 and 53 are removed through the discharge conduits 58, 59 and 60 ending within the common collecting manifold 61. The gaseous collecting within the upper part of the last reaction vessel 54 and still containing gaseous reagent are fed to the core of reaction vessel 51 through a conduit 56 which is positioned like conduit 55, close said stirring means 57.

The liquid mix which reacted with the gaseous reagent coming from conduit 56, is removed from the bottom of reaction vessel 51. Said liquid is made to pass through a heat exchanger 62 and then is fed to the core of reaction vessel 52 close to said stirring means 57, like conduit 55, by means of conduit 66.

Into reaction vessels 52, 53 and 54 are fed in parallel the gaseous reagent through conduit 63, 64 and 65, all of them being fed by a common manifold 66. Conduits 63, 64 and 65 discharge close to said stirring means 57, so as to ensure the largest dispersion of said gaseous reagent simultaneously to its entering the individual reac-

tion vessels. The amount of gaseous reagent entering the reaction vessels 52, 53 and 54 is substantially larger than the one entering the reactormixer 51; consequently, in reaction vessels 52, 53 and 54 occurs in a considerable way the deposition of the insoluble compounds due to the sulphonation of aromatic hydrocarbons, said insoluble compounds collecting on the bottom of the reaction vessels are removed therefrom, either periodically or continuously, through discharge conduits 67, 68 and 69 all opening into a common manifold 70.

The remaining mix of the liquid products which took part in the reaction, is removed from a higher level of the corresponding reaction vessel and fed into the core of the subsequent vessel through conduits 71 and 72, feeding the mix near said stirring means 57. Obviously, from the last reactor 54 the liquid mix, which took part in the reaction and is at this point completely purified, is removed from the device through a conduit 49, ready to undergo, when requested, further treatments.

From what is described above, it is clear that the excess of gaseous reagent fed through conduit 65 allows the complete reaction of the compounds which, through said reagent, are to be separated from the mass of the liquid mix.

On the other side, the re-use of said gaseous reagent in excess in the last reactor, through conduit 56, allows the recovery thereof, notwithstanding the presence of reagent in excess in the last stage of the reaction, the reaction effected in more steps requires the use of stoichiometric amounts of gaseous reagent.

FIG. 3 differs from the preceding one only because it is provided with means to deposit greater quantities of insoluble sulphonic compounds already in the reactor-mixer 151; that requires a conduit 167 for recovering said insoluble materials from the bottom of the first reaction vessel. At the same time, the liquid mix already treated in the first reactor is fed in series to the core of the second reaction vessel through a conduit 166. The other parts of the device shown in FIG. 3 operate in the same way as those shown in FIG. 2.

FIGS. 4 and 5 refer to the use of reaction vessels of the type shown in FIG. 6, whose constructive features will be described in details herebelow. Anyhow, it clearly appears that according to FIGS. 4 and 5 each reaction vessel is subdivided into an upper reaction zone 251' and a lower zone of decantation and separation 251''.

From the upper end of the separation zone 251'' is removed continuously the mix of liquid reagent which took part in the partial reaction with the gaseous reagent, and is recycled continuously in the upper part of the reaction chamber through a recycle conduit 73. As in the preceding FIG. 3, conduit 166 feeds the second reaction vessel and so on.

With the variation shown in FIG. 5, said recycle conduit 73' parts at a given point feeding a portion of the liquid taken from 251'' to the starting reaction vessel through conduit 73'', and a portion directly to the core of the subsequent reaction vessel through conduit 166'.

The most characteristic variation of the devices shown in FIGS. 4 and 5 is represented by the continuous recycle of the liquid mix of the compounds which have already partly reacted with the gaseous reagent and which have partly given away, through conduits 167, 68, 69, 67, the insoluble portion of the reaction product.

It is obvious that, according to a further variation, the recycle through conduit 73', 73'' may be restricted to the starting steps of the device.

With reference to FIG. 6, the reaction vessel shown therein is the second of the ones shown in FIG. 4. The upper part 252' comprises jackets 80,81 for controlling the temperature of the reaction vessel walls, and jackets 82, 83 are similarly provided for the lower zone of part 252''. In the lower part, the very reaction vessel 252' comprises a funnel part 84 ending with a cylindric conduit 85 which extends inside the deposit chamber 252'', so as to create an annular chamber 86 which receives the liquid mix separating from the insoluble sludges which deposited onto the bottom of part 252''.

In order to prevent the liquid jet mixed with insoluble acid sludge coming from 252', from causing a turbulence on the bottom of part 252'', and disturbing the deposit of the insoluble sludges, the cylindric body 85 widens in its lower part and opens in front of a transversal baffle 87 which prevents the fluid current coming down vertically, from mingling the deposited sludges with the liquid portion which just parted therefrom.

Numerals 88 denotes a recycle pump and 89 a shutter through which is controlled the outflow of the insoluble sludges through conduit 67. Said exchanger 90 cooperates with jackets 80 to 83 in keeping a temperature gradient between the deposit chamber 252'' and the very reaction chamber 252'. For the same purpose is intended the annular exchanger 91 arranged at the center of said cylindric pipe 85.

The choice between said two examples of device embodiments depends on the desired purity degree of the final product and on the starting composition of the material to be treated.

Besides, though the steps of the process in the figures have been shown as four, such a number is not a limit and may increase or decrease together with the apparatus power, the lowest number being two.

The following examples refer to FIGS. 2 to 6.

Example No. 3

The starting material has the following composition by weight:

normal paraffins	>98%
aromatic hydrocarbons	<1.2%
non-paraffinic hydrocarbons	<2%
sulphur contents	23 p.p.m.
at 15°C the specific weight of the starting material should be	0.760

The normal paraffins, according to the number of carbon atoms in the respective molecule, are distributed in such a manner:

C 10 =	1.4%
C 11 =	7.4%
C 12 =	10.5%
C 13 =	16.8%
C 14 =	14.6%
C 15 =	10.5%
C 16 =	9.8%
C 17 =	10.0%
C 18 =	8.9%
C 19 =	5.2%
C 20 =	2.7%
C >20 =	2.2%

Such a starting product is to be purified of the undesirable aromatic compounds by multiple step sulphonation according to the invention.

As gaseous reagent is used gaseous sulphur trioxide obtained from the combustion of molten sulphur and the subsequent transformation of SO₂ into SO₃ in presence of a catalyst. The gaseous mix will have the following volume composition:

SO ₃	=	7.0%
SO ₂	=	0.2%
N ₂ + O ₂	=	92.8%
		100.0%

The starting compound to be purified, of which only the sulphonable portion must react with the gaseous SO₃, will flow into the reactor-mixer 51 through conduit 55. The necessary amounts of SO₃, denoted by Q, is made to flow through conduits 63,64,65 into reactors 52,53,54 divided as follows:

0.65 × Q in the second reaction vessel;

0.25 × Q in the third reaction vessel

0.10 × Q in the fourth reaction vessel.

In the starting step device, such an amount of SO₃ is increased of 10%. The excess of gaseous reagent which has not reacted goes out of the reaction vessel 54 and is fed to the reactor 51.

According to the diagram shown in FIG. 2, by sulphonating 10% of the sulphonable compound dispersed in a large mass of non-sulphonable compound, in the first step there is not a substantial formation of insoluble acids.

Once the starting step of the device is ended, the feeding of SO₃ through conduits 63,64,65 returns to the stoichiometric amount. But, as from reaction vessel 51 arrives an aromatic compound already sulphonated to about 10%, it results that the last reaction vessel will always contain an excess of SO₃ which, being re-used through conduit 56, ensures the sulphonation of the last traces of aromatic hydrocarbon. Consequently, the portion of nonsulphonated aromatic hydrocarbons coming out through conduit 49 may be reduced to some dozens parts per million, as it appears from the underlisted final composition of the final product concerning the treatment of 100 kgs of starting compounds:

aromatic hydrocarbons	25 p.p.m.
sulphur	5 "
normal paraffins	98%
isoparaffins and cyclanes	2%
separated insoluble sludges	2 kgs
SO ₃ used	0.850 kgs

Example No. 4

Having a mix of paraffin base hydrocarbons with the following composition:

a) saturated hydrocarbons	80.9%
b) aromatic hydrocarbons	18.1%
c) compounds containing oxygen and sulphur	1.0%

by the process according to the invention the following products are obtained from 100 kgs of starting material:

purified saturated hydrocarbons	78.00 kgs
soluble petrosulphonates	15.50 kgs
insoluble sludges	20.00 kgs

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The sulphur trioxide used up is 13.75 kgs of which 2.70 kgs were used for obtaining soluble petrosulphonates with an average molecular weight of 460-470.

Examples No. 5

Having a mix of a cyclo-paraffinic base hydrocarbons with the following composition:

a) saturated hydrocarbons	82.00%
b) aromatic hydrocarbons	17.50%
c) compounds containing oxygen and sulphur	0.50%

by the process according to the invention the following products are obtained from 100 kgs of starting materials:

purified saturated hydrocarbons	78.50 kgs
soluble petrosulphonates	18.00 kgs
insoluble sludges	15.00 kgs

The sulphur trioxide used up is 11.62 kgs of which 3.15 kgs used for obtaining said soluble petrosulphonates.

It is to be understood that the invention is not limited to the examples shown. It is intended to cover all modifications and equivalents within the scope of the appended claims.

What we claim is:

1. A process for producing white oils and deo-kerosene from low boiling and high boiling crude oil fractions containing sulfonable aromatic components wherein high boiling crude oil fractions (A) having the following characteristics:

Average Molecular weight	315-400
Density	0.865 - 0.890
Kinematic Viscosity at 100°F	12 - 15 cts
Sulfonable Aromatic Compounds	up to 35 wt %
Boiling Point	above 320°C

are

a. mixed with low boiling crude oil fractions (B) having the following characteristics:

Boiling Point	120 - 280°C
Sulfonable Aromatic Compounds	up to 30 wt %

then

- sulfonating the resultant mixture by gaseous SO_3 ,
- separating and removing the resultant oil-insoluble sulfonic acid sludges,
- neutralizing the resultant liquid,
- extracting the oil-soluble sulfonic acids, and

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f. distilling the residual materials at temperatures in the range 120° - 280°C to obtain a deo-kerosene-type distillate product and a white oil bottoms product.

2. The process for removing the portion of aromatic compounds from a mix of hydrocarbons according to claim 1 which comprises the steps of separation of said aromatic hydrocarbons by sulphonation with a substantially stoichiometric amount of the sulfonation agent in at least two stages, traversed in series by the mix to be treated; and supplied, with the sulphonating agent in parallel, wherein said sulphonating agent is supplied in decreasing portions to the stages subsequent to the first one in parallel, and the excess of said sulphonating agent, removed from the last stage, is supplied to the first stage.

3. The process according to claim 1, wherein said gaseous SO_3 , proportioned in substantially stoichiometric quantities, is derived from the direct combustion of molten sulphur in air, and the catalytic transformation of the resultant SO_2 into SO_3 .

4. A process according to claim 1, wherein said gaseous SO_3 is diluted with an inert carrier gas.

5. A process according to claim 2, wherein said sulphonating agent is obtained by burning proportioned amounts of molten sulphur with amounts of air up to 1.1 - 1.5 of the stoichiometric quantity, and then transforming the SO_2 so obtained into SO_3 in a catalyst chamber.

6. A process according to claim 5, wherein the volume composition of said sulphonating agent is as follows:

SO_3	=	6	to	10.0%
SO_2	=	0.1	to	0.2%
$\text{N}_2 + \text{O}_2$	=	93.9	to	89.8%

7. The process according to claim 5, wherein said gaseous sulphonating agent is fed into the mix being treated and is dispersed therein by stirring thereby limiting the polysulphonation of the aromatic portion.

8. The process according to claim 2, wherein the feeding of the two reactants to each reaction step is accompanied by the removal of the insoluble products caused by the polysulphonation of the aromatic portion.

9. The process according to claim 2, wherein the portion of liquid treated in each individual stage, after separating therefrom the insoluble portions, is partially recycled.

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