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PROCESS FOR REFINING MINERAL OIL

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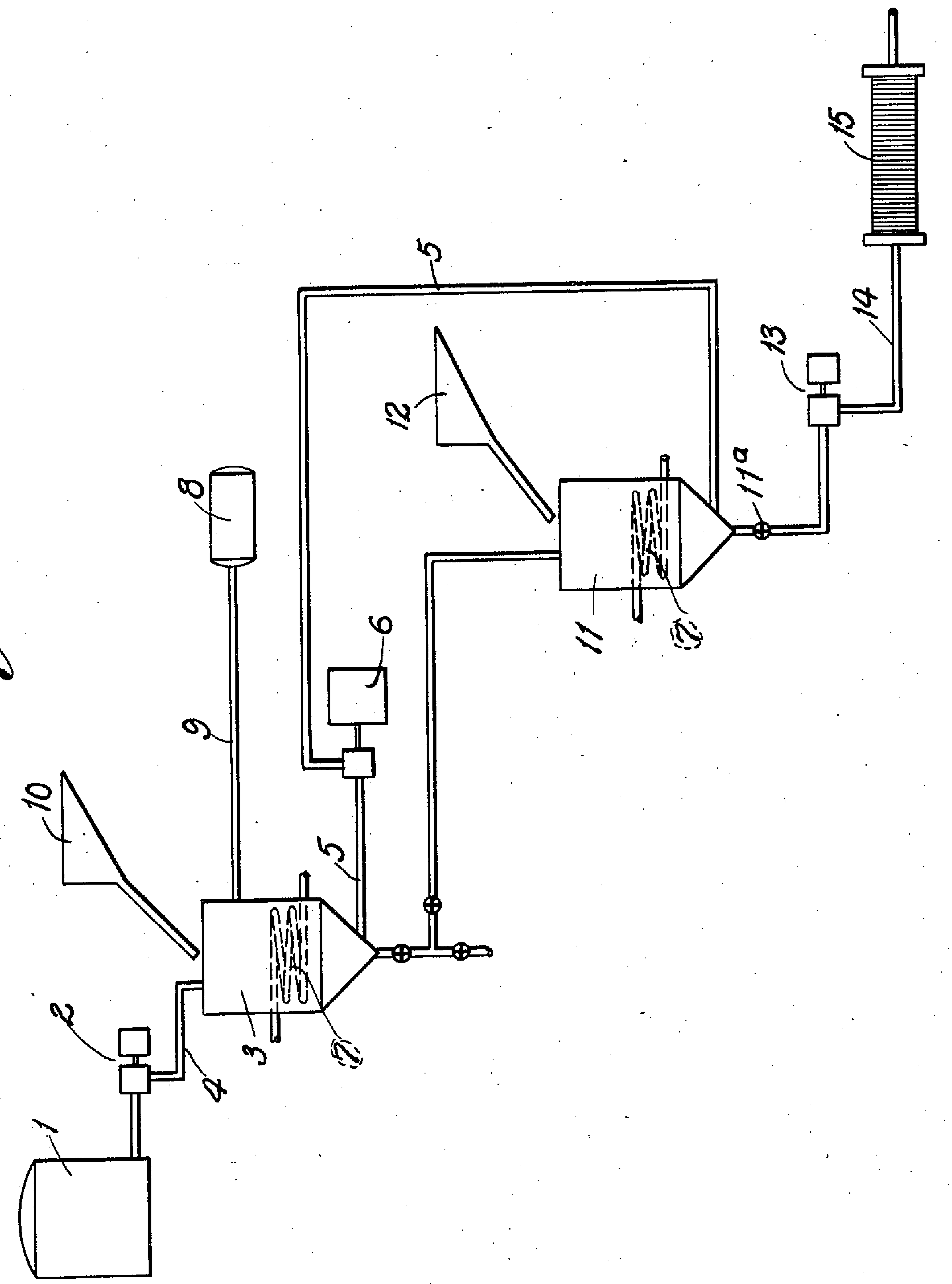
Fig. 1.



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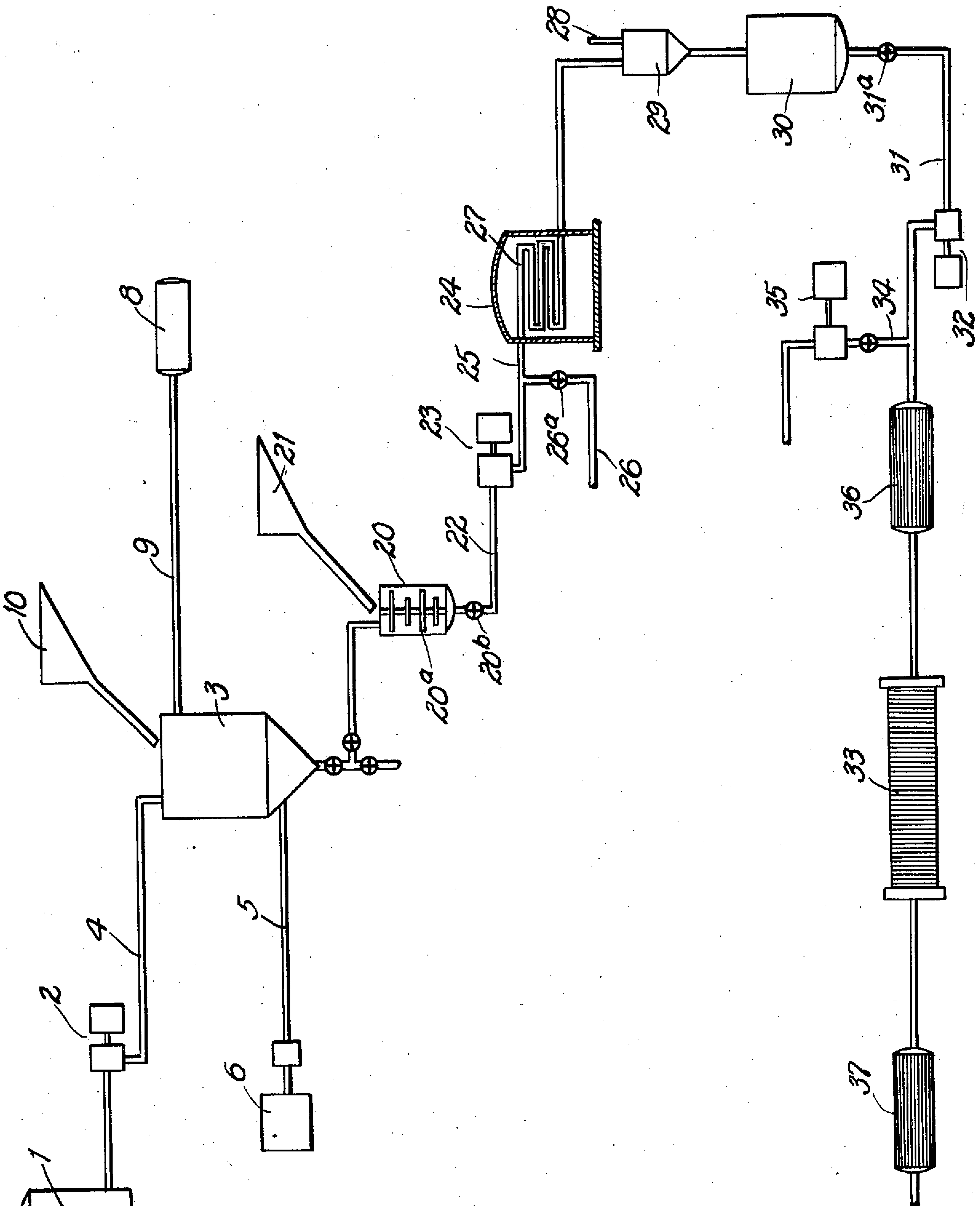

Fig. 2.

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PROCESS FOR REFINING MINERAL OIL

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14 Claims. (Cl. 196—41)

This invention relates to a process for refining, decolorizing and stabilizing the color of various kinds or grades of mineral oils, such, for example, as lubricating oil stocks, petroleum hydrocarbons, shale oil, mineral waxes, etc.

One object of our invention is to provide a process by which acid treated lubricating oil stocks can be rendered substantially free from suspended sludge without resorting to the procedure of washing the oil with water, steaming the oil, or subjecting the oil to the action of a mechanical separating device.

Another object is to provide procedure by which neutralized oil of stable color can be obtained from acid treated lubricating oils without the use of caustic solutions.

Another object is to provide a process by which acid sludge can be removed completely from acid treated oil without the necessity of heating the oil excessively.

Another object is to provide a process that will produce a clarified acidified oil which is of such a nature that when it is mixed with powdered adsorbent material to effect the decolorization of the oil, the subsequent separation of the oil from the spent adsorbent material can be easily accomplished.

And still another object is to provide a reliable and inexpensive process by which a decolorized oil of stable color, of improved outer-tone, and free from decomposition products, can be easily obtained from acid treated mineral oil.

In the art of refining, decolorizing and stabilizing the color of lubricating oil stock and other mineral oils it is common practice to mix the oil with strong sulfuric acid, and at the completion of the reaction, allow the treated oil to stand so as to permit the insoluble acid reaction product, commonly referred to as "acid sludge", to settle out as much as practicable. It is recognized that all of the acid sludge will not settle, but that a small portion remains suspended in the oil in the form of finely-divided particles commonly referred to as "pepper".

This "pepper" or fine particles of suspended acid sludge adversely affects the color of refined oil and renders the oil unstable. Various procedures have been employed and suggested for clarifying the oil at this stage in the operation of refining and decolorizing oil, but prior to our invention no process or procedure was known for completely eliminating the "pepper" from acid treated oil. The result is that refined oils produced by conventional procedure have a tendency to darken in color on standing.

In the process most commonly employed heretofore, the oil, after removal of the settled sludge, is thoroughly washed with water, which procedure eliminates most but not all of the suspended sludge, and also reduces the amount of free acid remaining in the oil. The oil is next washed with caustic solution to neutralize the remaining traces of acid, and it is again washed with water until free of alkalinity. Finally, the water in the remaining oil is driven off by blowing the oil with air, while the oil is maintained at a slightly elevated temperature. If further decolorization is desired, the oil is either percolated through a bed of granular decolorizing earth, or it is mixed with a finely ground, solid adsorbent material, with or without heating the mixture, and finally the oil is separated from the spent adsorbent material by filtering or by other means. The above described procedure is tedious, it is costly and it requires considerable time. Moreover, the oils ordinarily produced by such procedure will contain traces of soaps resulting from the action of the caustic solution on the traces of "pepper", or fine particles of acid sludge suspended in the oil. The presence of these soaps in the oil not only causes the oil to be unstable in color, but they also produce an undesirable bluish outer-tone or cast in the oil.

Attempts have been made to dispense with the first washing step and subsequent caustic washing, followed by additional washing with water, by substituting a step consisting of mixing the oil containing the suspended "pepper" with various amounts of powdered absorbent material, then heating the mixture to a temperature above 180° F., so as to decompose the "pepper" or fine particles of suspended acid sludge, and thereafter separating the oil from the admixed absorbent material. Powdered decolorizing adsorbents have also been used in this step which caused more or less reduction in the color of the treated oil in addition to the color reduction due only to acid treatment.

However, the oil produced by the procedure above described has a tendency to go off color on standing, even when the utmost precautions are taken to prevent oxidation of the oil while it is in a heated condition. We believe that the tendency for the oil to go off color is caused by the fact that all of the suspended sludge in the oil not only is not decomposed in the heating step, but that, under the action of the heat, some part of the sludge is re-dissolved in the oil, causing the oil to become unstable. On the other hand, if heat is not employed, the absorbent material does not completely remove the suspended sludge, resulting in a slimy mass which can only be separated from the oil with great difficulty, as it will not settle out of the oil with the main body of absorbent material and can be separated only very slowly in a filter press, even at great pressures, due to its slimy nature.

In our improved process, hereinafter described, it is not necessary to wash the oil with water to effect the removal of "pepper", or subject the oil to an excessively high temperature to effect the removal of acid sludge, for after the acid treated oil has been subjected to our treatment, it is substantially free from suspended sludge particles. Accordingly, our process is more rapid and less expensive to practice than conventional processes for refining and decolorizing mineral oils, as it eliminates the steps above mentioned. By completely eliminating the substance, to wit, "pepper", which is the cause of unstable color in refined oil, we obtain a product that is superior to the product obtained by conventional processes. And still another advantage or desirable feature of our process is that when the clarified acidified oil is mixed with powdered absorbent material, the subsequent separation of the oil from the spent absorbent material can be accomplished with ease, because of the absence of sludge.

The process that we have devised contemplates treating a mineral oil, such, for example, as lubricating stock, with strong sulfuric acid in the well known manner, by adding the desired quantity of acid to the oil and agitating the mixture in any suitable way, such as by blowing with air. The temperature of the oil during the acid treatment should be sufficiently high to afford good fluidity, so that an intimate contact between the acid and oil takes place. This temperature depends upon the grade of oil being treated and will vary from 90 to 100° F. for oils of the kind that are known to the trade as pale or red oil, and from 140 to 160° F. for oils of the kind that are known to the trade as cylinder stocks.

After an interval of agitation, and when the acid sludge begins to "break", a quantity of hydrated lime or similar metal hydrate is added to the mixture of oil and acid, preferably while the mixture is being agitated. When pale oil or red oil is being treated "breaking" of the acid sludge is clearly indicated by the formation of granular or flaky particles throughout the oil. After the hydrated lime has been added a gathering or consolidation of the sludge is usually immediately apparent, but if the action appears rather slow, additional quantities of the hydrate may be added.

In the case of cylinder stocks the procedure is somewhat different and is as follows:

The oil and acid mixture is subjected to agitation, as usual, until the acid sludge breaks and consolidates without the addition of any hydrated lime. This main body of sludge is allowed to settle from the oil and is removed. If the color of the remaining oil at this stage is not sufficiently reduced, it is then treated with an additional quantity of sulfuric acid in a similar manner and the main body of sludge is again allowed to settle and is removed. Thereafter, the remaining oil is agitated with hydrated lime, whereupon it will be found that the "pepper" remaining suspended in the oil is consolidated and will settle readily together with the lime. The reason for this difference in procedure between the treatment of cylinder stocks and the treatment of pale oil or red oil is due to the fact that in the case of cylinder stocks, a much larger amount of "pepper" remains suspended in the oil than in the case of pale or red oil. Hence, it becomes practicable to add the lime to the oil after the main body of sludge has been removed, resulting in the use of a lesser quantity of hydrated lime.

The quantity of lime used in either case should be sufficient to cause a complete deflocculation, but should never be sufficient to fully neutralize the free mineral acid or sulfur dioxide gaseous product of reaction remaining in the oil, as we find that subsequent further reduction in color by means of decolorizing adsorbent agent is greatly facilitated by leaving the oil in the acid condition at this stage. The amount of hydrate required also depends on the kind of oil treated and will vary from one-half to 2 lbs. per barrel of oil.

After the hydrate is added and when the sludge appears to be well formed, indicated by a definite breaking away from the oil and congealing in stringy masses, a point readily discernible to the practiced eye, agitation is stopped and the mixture of sludge and lime is allowed to settle from the oil. Contrary to the results ordinarily obtained, it will be found that in a comparatively short time the sludge has completely settled. leaving substantially no "pepper" suspended in the oil. The supernatant oil at this stage preferably will have acid reaction and smell strongly of sulfur dioxide.

After the sludge has thus completely settled, the oil is transferred to another container and is again agitated with air or by other convenient means. A quantity of powdered absorbent material, such as clay, infusorial earth, etc., is now added gradually to the agitating oil and simultaneously, if necessary, heat is applied to the mixture by any convenient means, in order to afford sufficient fluidity to the oil and the degree of heat may well correspond with that used on the oil during the acid treatment. Agitation is continued until the oil is neutral to chemical test and the odor of sulfur dioxide is no longer apparent. If the means of agitation is by blowing the oil with air or an inert gas, the elimination of the sulfur dioxide is much more rapid than by mechanical agitation. No harmful effects of the air on the respective oils have been noted at the temperatures stated. The quantity of absorbent material required to neutralize the oil will depend on the nature of the oil and the acidity remaining in the oil after acid treatment and will vary in amount from 2 lbs. to 20 lbs. per barrel of oil.

When the oil becomes neutral and when the sulfur dioxide has disappeared, the absorbent material with absorbed matters is separated from the oil either by settling or by any other well known or suitable means, such as by centrifuging, mechanical filters or by simply straining through a bed of sand or other filter material.

For absorbing material we use any powdered solid, such as clay, infusorial earth or similar substances. Any powdered decolorizing adsorbent, such as fuller's earth or similar natural decolorizing agent, or, it may be, any one of the well-known acid-treated earths may well be employed for neutralizing the acid-treated oil in place of the aforementioned clay, etc. In this case, a simultaneous neutralization and further decolorization of the oil is obtained, thus eliminating the bleaching step heretofore commonly resorted to when the acidified oil is neutralized by means of caustic solution, and it is desired to obtain additional reduction in the color of the oil. We have found that it is possible, especially in treating cylinder stock, to economize in the amount of decolorizing earth required to produce the desired reduction of color in the oil, by increasing the degree of heat applied to the mixture of acidified oil and powdered adsorbent agent. In this case the oil, after removing the sludge, is mixed with a powdered decolorizing agent, such as herein described. The mixture is then heated by any conventional means to a temperature preferably within substantially 50° F. of the flash point of the oil as determined by the Cleveland open cup tester. We find that at this temperature the reduction in color per unit weight of adsorbent is greatly increased.

We are aware that heating to these higher temperatures will, in some cases, substantially decompose or crack the oil, and we have found that heating alone or with the passage of an inert gas over the surface of the hot oil will carry off all decomposition products. However, we have also found that introduction of steam into the mixture while heating to these high temperatures will prevent any decomposition or cracking of the oil and aid in driving off sulfur dioxide and other volatile reaction products, and thus the color stability of the refined oil is not endangered. In heating to these higher temperatures we preferably use a closed system, so as to exclude air from contact with the oil. Otherwise, it is necessary to cool the oil below oxidizing temperatures before exposing it to contact with air. These temperatures range from approximately 150° F. for red and pale oils to 300° F. for heavy cylinder oil. However, and especially in case of heavy cylinder oils, it is of advantage not to cool the oil until after the filtering step, inasmuch as this step proceeds much more rapidly and efficiently at the higher temperatures, due to greater fluidity of the oil.

If, instead of filtering, it is desired to run the oil to a settling tank or otherwise expose it to the atmosphere after the heating step, it should be cooled without delay to a temperature at which oxidation would not occur. This is obvious to anyone skilled in the art and is only mentioned as a precaution necessary in practising our process.

Any suitable type or kind of apparatus may be used to practise our process.

Figure 1 of the accompanying drawings illustrates diagrammatically an apparatus that is particularly adapted for use in the treatment of lighter bodied oil, such as pale and red oil, or cylinder stock in a solution of naphtha, when temperatures below 180° F. are employed.

Figure 2 illustrates diagrammatically an apparatus that is particularly adapted for use in practising our process when temperature in excess of 180° F. are employed, the apparatus shown in this figure having the desirable characteristic of permitting the desired temperature to be attained quickly and having provision for venting the steam and excluding contact with air.

In practising our process with an apparatus of the kind shown in Figure 1, the raw oil, supplied from tank 1, is transferred by pump 2 into the acid-treating tank 3 through pipe 4. The oil is agitated by means of air supplied through pipe 5 by means of blower 6, and the temperature of the oil is increased, if necessary, to provide sufficient fluidity, by means of steam coil 7. At this point, and only if the oil contains water, on to five pounds of strong sulfuric acid per barrel of oil is added to the agitating oil, in order to absorb the water content of the oil, the acid being supplied from the acid egg 8 through pipe 9. After a thorough mixing, usually ten to fifteen minutes, air is shut off and the water acid settles from the oil and is withdrawn. Agitation is now resumed as before and additional sulfuric acid is introduced into the oil, sufficiently to produce the desired decolorization and purification of the oil. The amount of acid required depends on the quality and grade of oil being treated and ranges from 5 to 50 or more pounds per barrel of oil. Agitation continues until the insoluble tarry matter or sludge formed from the acid reaction begins to break from the oil in well defined flaky or stringy masses. At this point a quantity of hydrated lime, or other metallic hydrate in powder form is added to the agitated oil and acid mixture from hopper 10 and the agitation is continued until the sludge has definitely consolidated or "coked" from the oil, leaving the oil clear and free from "pepper" sludge. The amount of lime required varies, depending upon the kind of oil and amount of acid used, but preferably should be insufficient to fully neutralize the acidity of the oil.

Agitation is then discontinued and the sludge allowed to subside. The clear oil is next transferred to the second treating tank 11 and again agitated as in tank 3, heating, if necessary, to a temperature of proper fluidity, as before, this temperature ranging from 100° F. to 180° F., depending on the nature of the oil. Simultaneously a quantity of powdered earth, (clay, infusorial earth, fuller's earth, etc.) is added to the agitating oil from hopper 12. If the earth used has decolorizing power, substantial reduction in the color of the oil beyond that produced solely by the acid treatment will result. However, we find that with the clarified acidified oil produced by our improved process the use of an absorbent with or without decolorizing power will result in an oil of stable color. Agitation is continued until neutralization and the desired color reduction in the oil is attained, if necessary, adding a further quantity of powdered earth. At this stage there will be no odor of sulfur dioxide remaining in the oil. Valve 11a at the bottom of tank 11 is now opened and the oil-earth mixture is pumped by means of pump 13 and line 14 through filter press 15 to separate the absorbent material from the oil. Any other convenient means of separation may be employed, such as allowing the earth to settle to the bottom of the tank, or by using a centrifugal machine on the oil and earth mixture. The powdered earth should be dry, otherwise, the oil will receive moisture which will require elimination by heating the oil and blowing with air. The presence of excessive moisture in the oil also causes difficulty in passing the oil-earth mixture through a filter press.

The apparatus shown in Figure 2 can be used for treating any lubricating oil in accordance with our invention, but it is particularly adapted for treating heavy oils, such as cylinder stock. In the apparatus shown in Figure 2 any free moisture in the mixture can be eliminated by heating the mixture to temperatures in excess of 250° F. In using said apparatus the acid treating step, the addition of the hydrated lime or other equivalent material, and the subsequent settling of the sludge are the same as in the apparatus shown in Figure 1. The clear oil, in the acidified state, is discharged from the treating tank 3 into the mixer 20 and the required amount of powdered earth or other suitable material is also charged into the mixer 20 from the bin 21. Mixer 20 is provided with a mechanical stirrer 20a which causes intimate mixing of oil and earth. The mixture is continuously drawn from the bottom of mixer 20 through valve 20b and line 22 by means of pump 23 and charged to pipe furnace 24 through line 25. A small amount of high pressure steam is supplied to the mixture from a steam line 26 provided with a valve 26a. The mixture passes through heating coil 27 in the pipe furnace where it attains the desired temperature, which may vary, depending upon the kind of oil being treated, and may usually run from 350° to 500° F. The higher temperatures increase the rate of reaction and also, to some extent, the decolorizing power of the earth. The steam prevents any tendency of the oil to crack at the temperatures specified, and also prevents caking and local overheating in the coil. All steam and other volatile products are vented at 28 from vaporizer 29 and the oil-earth mixture passes by gravity to receiving tank 30, which is closed to prevent any access of air to the hot oil, and which may be steam-jacketed, if desired, to maintain sufficient fluidity of the oil to facilitate subsequent separation of the earth therefrom in a filter press.

The hot oil-earth mixture is next drawn from tank 30 through line 31 by means of pump 32 and charged to filter press 33, the line 31 being provided with a valve 31a. In the case of heavy cylinder oils, a stream of naphtha may be introduced, as shown at 34, by means of pressure pump 35, to provide sufficient fluidity to the oil to permit easy filtration. In this case the diluted oil mixture may be passed through a cooler 36 on the way to the filter press, if necessary, to prevent evaporation and loss of naphtha at the higher temperatures. The naphtha may be separated from the cylinder oil by subsequent distillation after the usual dewaxing step.

The filtered oil is finally cooled by a cooler 37 before exposure to the air, to prevent oxidation. The oil, treated as described, will be found constant in color, even after long period of storage and of great resistance to heat; also exhanced in appearance over the oils commonly produced by present methods.

While we have described the preferred way of carrying out our invention, we wish it to be understood that our broad idea consists in the use of hydrated lime or its equivalent to convert acid-treated oil into an oil that is free from suspended sludge, which treatment or procedure renders the oil more susceptible to subsequent neutralization and further reduction in color by the use of absorbent or adsorbent earths at the temperatures specified, with the use of steam to prevent decomposition of the oil when heated to the higher temperatures.

Having thus described our invention, what we desire to claim and secure by Letters Patent is:

1. A process for refining mineral oils and improving and stabilizing the color of same, characterized by distributing metal hydrate to acid-treated oil so as to effect the consolidation of the sludge without fully neutralizing the mineral acidity of the oil, settling the sludge, subjecting the clarified oil to treatment with a solid absorbent material in the presence of heat, and thereafter separating the neutralized oil from the absorbent material.

2. A process for refining, improving and stabilizing the color of mineral oils, which consists in treating raw oil with sulfuric acid, adding a metal hydrate to the oil and acid mixture in such quantities as to effect the consolidation of the sludge without fully neutralizing the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil, adding a powdered solid decolorizing agent to the clarified oil to neutralize and further decolorize the oil, heating the mixture to facilitate the reaction, and subsequently separating the decolorized and neutral oil from said agent.

3. A process for refining, improving and stabilizing the color of mineral oils, characterized by mixing a metal hydrate with acid-treated oil in such quantities as to cause consolidation of the sludge without fully neutralizing the mineral acidity of the oil, settling the sludge, subjecting the clarified oil to treatment with a powdered solid absorbent agent, introducing steam into the treated oil, then subjecting the oil to a temperature sufficient to promote rapid maximum reduction in color of the oil, and thereafter separating the oil from the absorbent agent used to treat the same.

4. In a process of the kind described in claim 3, the step of adding naphtha to the oil mixture while it is in a heated condition and prior to the final separating operation.

5. The process of refining mineral oils and improving and stabilizing the color thereof, consisting of treating the oil with sulfuric acid, adding hydrated lime to the oil and acid mixture to cause consolidation of the sludge, but insufficient to fully neutralize the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil, adding to the clarified oil a powdered solid decolorizing agent, to neutralize and further decolorize the oil, introducing steam into the mixture to prevent decomposition of the oil, heating the mixture to a temperature approximately within 50° F. of its flash point when tested in the Cleveland open cup and sufficient to promote rapid maximum reduction in color of the oil, partially cooling the hot mixture, and separating the spent earth from the decolorized and neutralized oil.

6. In the process described in claim 5, the steps of adding naphtha to the hot oil mixture, then separating the spent decolorizing agent and distilling the naphtha from the neutralized and decolorized oil.

7. The process of refining mineral oils and improving and stabilizing the color thereof, consisting of treating the oil with sulfuric acid, adding hydrated lime to the oil and acid mixture to cause consolidation of the sludge, but insufficient to fully neutralize the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil, adding to the clarified oil a powdered solid decolorizing agent to neutralize and further decolorize the oil, introducing steam into the mixture to prevent decomposition of the oil, heating the mixture in a substantially closed vessel to promote maximum rapid reaction, venting the steam and other volatile matters, and then separating the spent decolorizing agent from the decolorized and neutralized oil.

8. A process for refining mineral oils and improving and stabilizing the color of same, characterized by the step of intimately contacting the acid-treated oil with a treating agent consisting solely of lime in powdered form in sufficient quantity to cause complete deflocculation but not to fully neutralize the mineral acidity of

the oil and thereby effecting the removal of the "pepper" or fine suspended particles of sludge.

9. A process for refining mineral oils and improving and stabilizing the color of same, characterized by the step of subjecting acid-treated oil to the action of a treating agent consisting solely of a metal hydrate in sufficient quantity to cause complete deflocculation but not to fully neutralize the mineral acidity of the oil thereby causing consolidation of the sludge in the oil.

10. A process for refining mineral oils and improving and stabilizing the color of same, characterized by the steps of subjecting acid-treated oil to intimate contact with a treating agent consisting solely of a metal hydrate so as to effect consolidation of the sludge without fully neutralizing the mineral acidity of the oil, settling the sludge and subsequently treating the clarified oil with an absorbent medium.

11. A process for refining mineral oils and improving and stabilizing the color of same, characterized by the steps of subjecting the acid-treated oil to intimate contact with a treating agent consisting solely of a metal hydrate so as to effect the consolidation of the sludge without fully neutralizing the mineral acidity of the sludge, settling the sludge, subjecting the clarified oil to treatment with a medium that tends to neutralize and decolorize the oil and thereafter separating the oil from said medium.

12. A process for refining, improving and stabilizing the color of mineral oils, characterized by the steps of subjecting raw oil to an acid treatment, intimately contacting the acid-treated oil with a treating agent consisting solely of a metal hydrate in such quantities as to effect the consolidation of the sludge without fully neutralizing the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil from the sludge, and thereafter treating the clarified oil with a powdered solid absorbent agent.

13. The process of refining mineral oils and improving and stabilizing the color thereof, consisting of treating the oil with sulfuric acid, adding a metal hydrate to the oil and acid mixture to cause consolidation of the sludge, but insufficient to fully neutralize the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil, adding to the clarified oil a powdered solid decolorizing agent to neutralize and further decolorize the oil, introducing steam into the mixture to prevent decomposition of the oil, heating the mixture to a temperature approximately within 50° F. of its flash point when tested in the Cleveland open cut and sufficient to promote rapid maximum reduction in color of the oil, partially cooling the hot mixture, and separating the spent earth from the decolorized and neutralized oil.

14. The process of refining mineral oils and improving and stabilizing the color thereof, consisting of treating the oil with sulfuric acid, adding a metal hydrate to the oil and acid mixture to cause consolidation of the sludge, but insufficient to fully neutralize the mineral acidity of the oil, settling the sludge, removing the supernatant clarified oil, adding to the clarified oil a powdered solid decolorizing agent to neutralize and further decolorize the oil, introducing steam into the mixture to prevent decomposition of the oil, heating the mixture in a substantially closed vessel to promote maximum rapid reaction, venting the steam and other volatile matters, and then separating the spent decolorizing agent from the decolorized and neutralized oil.

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