METHOD OF DECOLORIZING A MINERAL OIL

Filed Jan. 15, 1940
METHOD OF DECOLORIZING A MINERAL OIL


Application January 15, 1940, Serial No. 313,878

14 Claims. (Cl. 196—147)

This invention relates to the refining of mineral oils, and more particularly, to the decolorizing of the same.

The invention provides an efficient and relatively inexpensive process for the continuous decolorization of mineral oils and the continuous recovery, reactivation and cyclic re-use of the materials used in, and in connection with, the decolorization of oils. The invention comprehends the improved cyclic decolorizing process as a whole and also several specific parts thereof.

Numerous processes have been proposed heretofore and are now in commercial use in which mineral oils are subjected to the action of decolorizing earths, that is, earths which have the property of removing objectionable coloring matter from such oils. In general these processes employ elevated temperatures in order to obtain efficient contact between oil and decolorizing earth, and many of these processes effect such contact in the presence of oxidizing atmospheres, such as air. Such processes employing elevated temperatures generally in the neighborhood of about 500°—650° F., whether conducted in an oxidizing atmosphere either intentionally or due to the presence of adventitious air or air liberated from the grains of earth by the elevated temperatures, promote oxidation of the treated oil and of the coloring matter removed from the oil by the decolorizing earth. Oxidation of the treated oil is an obvious objection to these processes. Moreover modification of the coloring matter removed from the oil and adsorbed by the decolorizing earth which occurs at the elevated temperatures employed in such processes, and which is promoted by oxidation, prevents or renders impracticable reactivation of the spent earth with solvents. In the few instances where reactivation of spent decolorizing earth may be accomplished with solvents large and complex mixtures of expensive solvents are required, and even then the reactivated earth is not restored to its original high decolorizing efficiency. Reactivation of spent decolorizing earth is necessary if such decolorizing processes are to be commercially feasible. Regeneration of spent earth by burning such earth to restore its decolorizing efficiency is accompanied by destruction of the grains of earth with the production of an excessive quantity of earth too fine for efficient oil-earth separation. Moreover, when such earths regenerated by burning are cooled, air is absorbed by the grains of earth and this air is subsequently liberated in situ in the oil by the elevated temperatures employed in the decolorizing operations.

Proposals for decolorizing viscous mineral oils have been advanced which involve subjecting such an oil diluted with a solvent therefor to the action of a decolorizing earth at a temperature not substantially in excess of about 200° F., reactivating the spent earth separated from the decolorized oil by subjecting it to the action of a solvent capable of extracting from the earth the coloring matter removed from the oil by the earth, thereafter displacing the color solvent with an oil solvent and thereafter again using the reactivated earth in the decolorizing treatment without intervening reduction of the earth to dryness. However such processes require the use of approximately equal proportions of diluent when the oil being treated is an oil of relatively high viscosity, such, for example, as a dewaxed raffinate from a Pennsylvania cylinder stock. Furthermore, such processes involve, stripping of the oil solvent from the decolorized oil after separation from the decolorizing earth and this stripping operation, particularly when applied to unstable oils such as Pennsylvania neutral oils which have not been refined by solvent extraction, tends to throw the treated oil off color thus requiring an additional operation in which the stripped decolorized oil is subjected to contact with a fresh decolorizing earth to restore the brightness of the oil. Processes of this type have the further disadvantage that the activity of decolorizing earths is greatly reduced at temperatures approximating 200° F., and this circumstance not only increases the amount of decolorizing agent required to treat a given amount of oil but also involves an increase in the size and cost of the equipment employed to carry out the decolorizing and reactivating operations together with a corresponding increase in the materials used in the reactivating treatment.

We have devised a novel process whereby mineral oils may be decolorized with decolorizing earths at moderately high temperatures, for example 350°—450° F., with efficient and effective solvent reactivation of the decolorizing earth and with efficient and effective cyclic re-use of the decolorizing earth and the materials used in its reactivation. In our improved process the naphtha, or equivalent oil solvent, which is present during the contact treatment in a proportion considerably smaller than that involved in the low temperature decolorizing processes heretofore proposed, is stripped from the treated oil in the presence of the decolorizing earth and the oil is
subsequently separated from the earth as a finished product, the final separation being preferably accomplished in a non-oxidizing atmosphere and at a temperature below the maximum required to supply all of the heat necessary to accomplish the stripping. Thus even in its simplest form our process eliminates the necessity of the final brightening treatment which normally is required to offset the effects of the usual final stripping treatment. Moreover, in our process the heating applied to obtain efficient and rapid action of the decolorizing agent is utilized in a particularly advantageous manner to effect stripping of the oil from the decolorized oil.

Our process also makes it possible to utilize the contact heater normally employed to effect the final heating in the decolorizing operation proper, for recovering, in finished form, oil initially retained by and subsequently washed from the spent earth and the oil solvent by which the washing is effected, and also for reducing the burden on the color solvent recovery unit. Thus our invention not only provides for efficient use of the decolorizing earth and the materials used in its reactivation with a corresponding reduction in the requirements for such materials, but it also provides for the efficient use of the equipment involved, both by reducing the size of the various elements and by enabling certain elements simultaneously to perform several functions that heretofore have required separate additional equipment.

According to our process the oil to be decolorized is thoroughly admixed with a slurry of decolorizing earth and naphtha, or equivalent oil solvent, in a contact heater feed tank wherein it is preferably preheated to a temperature of 150°-250° F. This mixture is then passed through a contact heater, which may comprise a direct fired pipe still or pipe stills, in which the temperature of the mixture is raised to an outlet temperature sufficiently high to supply the heat necessary to accomplish stripping of the oil solvent from the mixture and to enable the decolorizing earth to exert an efficient and rapid decolorizing action but low enough to avoid modification of the coloring matter adsorbed by the earth to such an extent as to prejudice substantially complete reactivation of the earth by the used color solvents. An outlet temperature of 350°-450° F and preferably 400°-425° F accomplishes these objectives with most oils. The heated mixture leaving the contact heater then passes to a vapor separating or stripping zone wherein the oil solvent and any trace of color solvent that may have been retained in the reactivated earth are separated from the earth oil mixture. The stripping advantageously is accomplished in two stages, the second stage being conducted at reduced pressure in order to avoid the necessity of using too high an outlet temperature in the contact heater. The use of two stages in the stripping operation has the further advantage that the color solvent may be stripped in the first stage, whereupon steam may be employed in the second stage to assist in completing stripping of the oil solvent without contaminating the color solvents with such. The earth is then separated, by filtration, from the stripped earth-oil mixture at a temperature sufficiently high to permit a rapid filter rate but preferably appreciably lower than the maximum temperature attained in the contact heater. If the viscosity of the oil being treated is high enough to require relatively elevated temperatures in order to obtain a desirable filter rate, the separation should be made in a non-oxidizing atmosphere.

Since stripping of all volatile materials is necessary to reduce the oil to the desired flash, fire and viscosity characteristics is accomplished in our process in the presence of the decolorizing earth, subsequent separation of the earth from the oil leaves the latter in the form of a finished product requiring no additional stripping treatment to obtain the desired flash, fire and viscosity characteristics and no additional decolorizing treatment to offset the adverse effects of the usual final stripping operation on the brightness of the oil.

In accordance with our invention the spent earth separated by filtration from the finished oil may then be subjected to recovery treatment in the following manner. The separated earth is slurried with naphtha, or an equivalent oil solvent and filtered to remove oil held by the earth, and the oil-solvent mixture thus obtained may be treated to recover its component parts by merely introducing it into the previously mentioned contact heater feed tank from which it passes through the contact heater and stripping zone thereby recovering both the naphtha component and the oil component of the latter in finished form, without separate recovery equipment or separate recovery treatment. The substantially oil-free spent earth is then extracted with a suitable solvent for adsorbing coloring matter, such as methyl ethyl ketone, filtered, washed with an additional quantity of naphtha or equivalent oil solvent to displace at least the major portion of the color solvent retained by the earth and further filtered. The reactivated earth in the form of a filter cake wet with naphtha, and containing any color solvent not removed from the filter cake by the last-mentioned naphtha washing, is then admixed with sufficient additional naphtha, or equivalent oil-solvent, to form a pumpable slurry and this slurry is returned to the contact heater feed tank for use in the decolorizing treatment of additional oil. This oil-earth-solvent mixture then passes through the contact heater and stripping zones as previously described.

Naphtha and retained color solvent removed by stripping of the hot mixture from the contact heater for the decolorizing operation is preferably used to supply, at least in part, the naphtha used in preparing the final slurry of reactivated earth and in displacing color solvent from the earth following the extraction treatment. By this method of recovering naphtha and traces of color solvent not displaced from the reactivated earth by the final naphtha washing, the burden on the color solvent recovery unit may be somewhat reduced. In fact the contact heater for the decolorizing operation proper and the ensuing stripping operation in a sense become the final stage of the reactivating treatment.

The process of the invention is especially adapted for continuous operation and may be made entirely continuous if finished oil filters, such as Oliver continuous drum type precoat filters, are used. In this process the reactivating treatment restores the decolorizing earth to a decolorizing efficiency very closely approaching that of fresh decolorizing earth so that the cyclic procedure may be carried out over considerable periods of time without adding fresh decolorizing earth to, or purging spent decolorizing earth from, the system. However, as the de-
colorizing efficiency of the earth will gradually decrease, fresh earth may be supplied to and spent earth purified from this system by either of several methods which will be hereinafter more fully described.

The process of our invention is applicable to the decolorization of mineral oils generally and petroleum lubricating oils in particular. It is especially useful in the decolorization of Pennsylvania oils, many of which are notoriously unstable with respect to their color, ranging from non-viscous neutral oils through the regular neutral oils to viscous oils such as cylinder stocks. It may be used in the treatment of petroleum lubricating oils either before or subsequent to the dewaxing or other refining of such oils. It is especially useful in the treatment of oils of relatively high viscosity such, for example, as a dewaxed raffinate from a Pennsylvania cylinder stock.

The oil solvents useful in our process include any of the various solvents generally used for this purpose. It is only necessary that the oil solvent be capable of dissolving oil, sufficiently volatile to be completely separable from the oil by distillation at relatively low temperatures, particularly separable by distillation from the color solvent, and that it have in itself substantially no solvent capacity for coloring matter adsorbed from the oil in the earth. We have found that naphtha having an initial boiling point of 230° F. and an end point of 350° F. is particularly adapted for use in our process. Commercial naphthas known as 200/300 or 300/400 naphthas may also be used with advantage. The proportion of naphtha present in the mixture subjected to the decolorizing operation proper may vary widely although in most instances it will be substantially less than that required in the low temperature decolorizing operations previously proposed. Thus in the treatment of Pennsylvania neutrals using that form of operation in which the reactivated earth from the reactivating filter is slurried with only enough naphtha to render it pumpable before introduction into the contact heater feed tank, the percentage of naphtha to oil may be as low as 5% by volume on the oil naphtha blend. On the other hand when decolorizing raffinates of the type mentioned above and employing that form of operation in which the lighter naphtha washings from the decoloring operation are introduced to the contact heater feed tank for recovery of the oil removed from the spent earth, the proportion of naphtha in the oil naphtha blend in the decolorizing operation proper may vary from about 40% to 60% or even higher.

A wide variety of finely divided decolorizing earths may be used in carrying out the process of our invention. For example, finely divided fuller's earth, activated bauxites, such as "Porcel" and acid-treated bentonites, such as "Piltrol," or "Tonsil," may be used. We have found, however, that the synthetic adsorbent decolorizing earth known as "Magnesol" may be used with particular advantage. "Magnesol" is a synthetic hydrated magnesium silicate normally obtained by first preparing a hydrated calcium silicate and then reacting the calcium silicate with magnesium chloride. If "Magnesol" is used, from 2% to about 12% of the decolorizing earth on a dry basis by weight of oil treated may be used with advantage. We have found 5% to 12% of "Magnesol" to be particularly advantageous in decolorizing raffinates of high viscosity of the type previously mentioned. These percentages are based on using the new clay. These percentages will be somewhat increased when using reactivated clay, the increase depending upon the decolorizing efficiency of the reactivated clay. Within the temperature range of 400° F. to 425° F., this type of clay has approximately twice the efficiency and decolorizing action as that exerted at temperatures approximating 200° F.

We have investigated numerous color solvents for removing from the decolorizing earth coloring matter adsorbed from the oil, and have found that the lower alcohols and ketones may in our process be used for this purpose with advantage. Thus, methyl, ethyl and isopropyl alcohols and such ketones as acetone, methyl ethyl ketone, methyl propyl ketone and methyl isopropyl ketone may be used advantageously. These solvents either alone or in combination, and preferably in further admixture with naphthas or equivalent oil solvent, have been found to be particularly efficient in the process of our invention. A mixture of one part of methyl ethyl ketone and two parts naphtha by volume has been found to be particularly effective. The above-mentioned color solvents effect removal of coloring matter from spent decolorizing earth at temperatures ranging from atmospheric temperature to about 150° F., or somewhat higher. However, we have found especially efficient results to be obtainable with an extraction temperature of about 130° F.

Other specific features and specific advantages of our invention will be apparent from the following more detailed description of our process with reference to the accompanying schematic drawing. In this further description of our process we will describe, for the purpose of illustration, embodiments of the invention in which "Magnesol" is used as the decolorizing earth, in which naphtha is used as the oil solvent and in which a solvent blend comprising one-third methyl ethyl ketone and two-thirds naphtha is used as the color solvent. In the drawing the flow of various materials through the system is shown by composite lines designed to show particular components of the mixture present in various parts of the system. The composite lines are intended to illustrate that lines carrying the indicated components and will be so referred to herein.

Oil to be decolorized, preferably preheated to a temperature of 150° F.-200° F. or higher, is introduced through line 1 into contact heater feed tank 2 of the enclosed type. The oil is mixed in this tank with naphtha and with activated decolorizing earth in amounts and from sources hereinafter more fully discussed. Continuous mixing and contact is provided by conventional mechanical stirring means assisted, if desired, by recirculation from the bottom to the top of the tank by means of a circulating pump. The earth-oil-naphtha mixture, in the form of a slurry, is delivered through line 3 into contact heater or heaters 4. In the contact heater, which may comprise a direct fired pipe still or pipe stills, the temperature of the earth-oil-naphtha mixture is raised to an outlet temperature of about 400°-425° F. Under these conditions the oil under treatment is substantially completely decolorized (i.e., brought to the desired color) by the time the mixture reaches the outlet of the heater 4. When more than one heater is employed the heaters may be arranged either in series or in parallel. The hot mix-
ture is then delivered through line 5 into flash tower #1 indicated by numeral 6 on the drawing.

Flash tower #1 is the initial vapor separating zone of the two stage stripping operation. In our preferred method of operation this tower is operated at substantially atmospheric pressure and separates the heated mixture charged to the tower into two products, an overhead fraction and a residual fraction. The overhead product is taken off as vapor through an appropriate condenser and then passes through line 7. This product comprises a major part, usually about one-half of the naphtha contained in the mixture leaving the contact heater together with any color solvent present in this mixture. If this overhead product contains a fairly high percentage of color solvent, as may be the case when the naphtha content of the mixture supplied to the contact heater is low, it may be supplied to the color solvent recovery unit 52 through line 9. Otherwise it is discharged into line 42. The other product obtained from flash tower #1, the bottoms from this tower, consists of the decolorized oil and the earth contained in the charge from the contact heater 4 together with naphtha not removed in the overhead from this tower. This oil-earth product passes through line 8 into flash tower #2 indicated by numeral 10 on the drawing.

Flash tower #2 comprises the second vapor separating zone of the two stage stripping operation. In accordance with our now preferred method of operation, this tower is maintained under a subatmospheric pressure in order to assist stripping from the mixture of the last traces of the naphtha remaining therein. Direct steam or inert gas such as flue gas may be introduced into flash tower #2 to further reduce the partial pressure and assist in this stripping operation. Although moisture is a contaminant for most color solvents, direct steam may be used in the #2 flash tower to assist the final stripping because any color solvent originally present in the mixture has been taken off overhead from flash tower #1. Two products are also obtained from this flash tower, an overhead fraction and a bottom fraction. The overhead fraction, taken off in vapor form, includes all of the naphtha originally present in the mixture and not vaporized in the #1 flash tower and any moisture that enters the tower by virtue of the introduction of flue gases or direct steam thereto. After suitable condensation in a conventional condenser, and separation of the condensed moisture in a conventional separator, the stripped naphtha passes through lines 11 and 56 to a naphtha storage tank 25. The bottoms from flash tower #2, consisting of decolorized oil and earth freed from naphtha, are delivered through line 12 into filter feed tank 13 of the enclosed type. Flash tower #2 is preferably controlled so that the oil-earth mixture leaving the bottom of this tower will have a temperature of from about 250° F. to about 350° F. depending upon the viscosity of the oil, higher temperatures being used for oils of higher viscosity.

The hot mixture of decolorized oil and spent decolorizing earth, then passes, preferably continuously, through line 14 to decolorized oil filter unit 15 of the enclosed type. This filter unit may comprise one or a plurality of conventional batch or rotary drum-type vacuum or pressure filters operating at a temperature ranging from about 250° to about 350° F. These somewhat elevated temperatures promote high filter rates, particularly with oils of relatively high viscosities. Spent earth is separated from the decolorized oil in filter unit 15 with the production of a filtrate comprising decolorized oil and a filter cake. The filtrate is discharged through line 16, preferably with additional cooling to a temperature of about 140° to 160° F., to a storage vessel 17 of the enclosed type. Additional cooling at this point is desirable to preclude the oil being thrown off color through oxidation by adventitious air or through prolonged exposure, in the absence of the decolorizing earth, to the relatively high temperature used to promote high filter rates in the decolorized oil filter unit. If the decolorized oil is cloudy due to the presence of a small amount of fine earth this cloudiness may be removed by passing the oil through a conventional blotting press serving as a strainer. The filter cake, obtained at a temperature of about 250° to 500° F., or somewhat higher, comprises about 55% by weight of oil and about 45% of earth when obtained from a batch-type filter such as that known as a Sweetland filter and comprises about 50% by weight of oil and about 47% by weight of earth when obtained with a continuous-type filter such as that known as an Oliver press filter. The filter is blown with a non-oxidizing gas to displace excess oil from the filter shell and earth cake, and the filter cake of spent earth, containing the coloring matter removed from the oil by the earth, then is dropped in the usual manner. This filter cake is then delivered through a suitable chute or the like designated by line 18 into a slurry mix tank 20 of the enclosed type. A minor amount of the filtrate from the decolorized oil filter unit is withdrawn from storage tank 17 through line 21 and introduced into tank 20 so as to produce, with the assistance of appropriate agitation, a pumpable slurry of the spent earth filter cake.

This mixture usually will form a pumpable slurry if the oil content is increased to about 63-65% by weight. The elevated temperature of this earth slurry enhances its pumpability. The slurry produced in mix tank 20 is then introduced through line 22 into naphtha mix tank 23 of the enclosed type wherein enough naphtha is added to the mixture to produce a final slurry containing about 20-25% by weight of spent earth on a dry basis and about 80-75% by weight of oil and naphtha. This slurry is then introduced, preferably continuously, through line 24 into deoiling filter unit 29 of the enclosed type which may comprise one or a plurality of rotary drum-type vacuum or pressure filters operated at temperatures ranging between 130° F. to about 200° F., higher temperatures promoting higher solubilities of oil in naphtha and also higher filtering rates. The filter cake obtained in filter unit 25 is washed with naphtha supplied from naphtha storage tank 26 through line 27, and preferably preheated to a temperature of from about 130° F. to about 200° F., depending upon the temperature to be maintained in the deoiling filter unit 25, in order to remove as much oil from the spent earth as is practical. The first filtrate obtained from the deoiling filter comprising wash naphtha containing from about 90% to about 95% or more of the decolorized oil retained in the spent earth is then discharged from the decolorized oil filter unit 16, is delivered through line 28 to filtrate receiver #1 of the enclosed type designated by numeral 29 on the drawing. Filtrate collected in receiver
filter 41, comprising reactivated earth of high efficiency and containing about an equal amount of naphtha and from 0.5% to 1.5% of color solvent, is removed through a scroll, or the like, indicated by numeral 43 on the drawing and is charged to reactivated earth slurry mix tank 45 of the enclosed type wherein it is worked up into a thick pumpable slurry with additional naphtha, obtained from flash tower #1 through line 7, line 42 and branch line 46, or from the color solvent recovery unit through line 55 if the overhead from flash tower #1 is being supplied to the color solvent recovery unit through line 9. The slurry thus obtained, containing about 28-30% by weight of earth on a dry basis, and the balance essentially of naphtha, is then delivered through line 41 into contact heater feed tank 2 as the source of decolorizing earth, and at least in part the source of the naphtha, to be admixed with oil to be decolorized to form the earth-oil naphtha mixture that supplies the contact heater.

The composite mixture thus charged to feed tank 2 through lines 1, 30 and 41 as a variable percentage of naphtha, the oil to be decolorized, minor traces of color solvent and about 2-16% of earth on a dry basis by weight of the oil component depending upon the kind of oil and the decolorizing efficiency of the earth.

The first filtrate from reactivating filter 41, comprising most of the color solvent together with wash naphtha, is discharged through line 48 into filtrate receiver #1 of the enclosed type designated by numeral 50 on the drawing and preferably maintained under a vacuum to assist filtration in unit 41. The color solvent admixed with wash naphtha is delivered through line 51 to a suitable color solvent recovery unit 52 in which coloring matter removed from the treated oil by the earth and dissolved out of the earth by the color solvent is removed and discarded. The recovered blend of color solvent and an appropriate quantity of naphtha to make up the desired color solvent blend is discharged from the solvent recovery unit through line 53 into storage tank 54 of the enclosed type. Naphtha in excess of that desired in the color solvent blend and in excess of that drawn from storage tank 54 for use in extractor 37 is discharged from the solvent recovery unit through line 55 either for use as the supply of naphtha drawn through line 42 or for return to naphtha storage tank 26 through line 56. The final naphtha wash from reactivating filter 41, comprising substantially only naphtha, is discharged from reactivating filter 41 through line 57 into filtrate receiver #2 of the enclosed type designated by numeral 55 on the drawing and also preferably maintained under a vacuum to assist filtration in unit 41. This naphtha may be returned through line 60 into spent earth slurry mix tank 35 as the source of naphtha used in working up the spent earth into a slurry in this tank.

As the decolorizing efficiency of the reactivated earth in the procedure above described is high, the process may be operated in a continuous manner over considerable periods of time without adding fresh decolorizing earth to or purging spent decolorizing earth from the system. However, fresh earth may be added and spent earth naphtha mother of the following procedures. The first method involves continuing the cyclic operation until the decolorizing efficiency of the earth has gradually fallen to a point where its efficiency is undesirably low and then voiding all of the earth from the system and...
replacing the spent earth thus voided with new earth. When this is done the spent earth is advantageously voided from the system after de-colling in de-colling filter unit 25. At this point the earth is in the form of a naphtha-earth cake. This earth may be slurried with enough naphtha to render it pumpable and the slurry then pumped to a conventional type of filter and the earth cake there formed may be steamed to recover at least a major portion of the naphtha. While the spent earth is being voided from the system in this manner there is no flow of naphtha-earth cake from the spent earth slurry mix tank 35 through line 36 to spent earth extractor 37 and on to reactivating earth filter 41, and therefore no naphtha-earth cake is passing from the re-activating filter 41 so that no trace of color solvent will be present in the material passing to the contact heater feed tank 2. In order to keep the contacting portion of the unit operating during this period, new decolorizing earth may be introduced into contact heater feed tank 2 and there slurried with a mixture of the oil to be decolorized and the first naphtha washings from the de-colling filter which accumulate in the filtrate receiver 29. Any moisture contained in this fresh earth will be driven off in the #1 flash tower and subsequently separated from the naphtha present in the overhead from this tower before introduction of such naphtha into the system through line 7. The presence of moisture in the overhead from the #1 flash tower during this period is not objectionable for the reason that no filter cake is passing from the reactivating filter during this period and therefore no color solvent will be present in the #1 flash tower overhead to be contaminated by the moisture.

The second method of introducing new earth to the system involves voiding a definite percentage of the spent earth from the system continuously, such spent earth preferably being voided after the de-colling filter unit 25 as above described, and continuously supplying a corresponding percentage of fresh earth so as to maintain the average efficiency of the reactivated earth above a predetermined value. The amount of spent earth thus voided and fresh earth simultaneously supplied may vary from 2 to 10% or somewhat higher. In this method of operation the fresh earth advantageously may be introduced either into line 8 between the #1 and #2 flash towers or into the bottom of the #2 flash tower. In this method of operation the moisture contained in the fresh earth will be distilled overhead from the #2 flash tower along with the steam used to assist stripping in this tower. New “Magnesol” containing from 10% to 20% free moisture and it will be noted that in both of the alternative methods for introducing fresh earth to the system as above described, the new earth is substantially dehydrated before it can carry appreciable quantities of moisture into the color solvent when the earth and color solvent come together in the extractor 37.

All operations of our process employing elevated temperatures and carried out in apparatus of the enclosed type, particularly those in which volatile solvents are present, are provided with an atmosphere of an inert or non-oxidizing gas such, for example, as flue gas. This may be accomplished with particular advantage by providing three systems for supplying such inert atmospheres, one system including operations in which naphtha, or an equivalent oil solvent, is the only volatile liquid present, the second system including operations in which the color solvent is present in an appreciable quantity, and the third system providing a non-oxidizing atmosphere in the filter feed tank 13 and decolorized oil filter where no volatile liquid is present. The mixture contained in the filter feed tank 13 and in the decolorized oil filter unit is maintained at temperatures in the range of about 250° F. to about 360° F. and therefore should be protected against oxidation. However, the presence of naphtha or color solvent vapors would throw off the flash point of the decolorized oil obtained from decolorizing oil filter unit 15. If desired, the system for providing non-oxidizing atmospheres in those parts of the cycle of the cyclic system wherein volatile liquid is present may be combined. Each of the systems for providing non-oxidizing atmospheres may be provided with appropriate foam traps, gas holders, heaters and pumps. The inert gases circulated through various parts of the system in addition to preventing fire hazard and the absence of flammable mixtures of solvent vapors and low enough to avoid oxidation of the oil and removed coloring matter even in the presence of air.

As the oil solvent present during the earth contact treatment is removed from the oil in our process in the presence of a decolorizing earth and the oil is recovered in finished form requiring no further treatment upon separation of the earth, our processes make it possible to produce in a single contact treatment, and notwithstanding the presence of oil solvent and even traces of color solvent in the mixture charged to the decolorizing step, an adequately decolorized oil having flash, fire and viscosity characteristics substantially identical with the original oil charged to the process. Further, the use of moderately elevated but limited temperatures in our process makes possible an increase of substantially 100% in the efficiency of the decolorizing earth as compared to prior processes involving decolorization in dilution at relatively low temperatures. The resulting 50% reduction in the earth requirements corresponding reduces the requirements for wash naphtha, color solvent, filter units and other reactivating equipment in addition to increasing the amount of oil that may be treated with a given amount of decolorizing earth. At the same time the use of moderately elevated temperatures makes possible stripping of the volatile solvents by the heat supplied to complete the decolorizing treatment while the limitation of the maximum temperature attained and the use of inert atmospheres avoids modification of the coloring matter adsorbed from the oil in such a manner as to elongate the grains of the earth and preclude reactivation of the spent earth with limited quantities of color solvent.

Furthermore, since our process utilizes reactivated earth wet with oil solvent from the reactivating filter cake and avoids the necessity of reducing the reactivated earth to a dry condition as a part of the reactivating treatment, it avoids the deterioration and breaking down of the grains of decolorizing earth by the elevated temperature employed in conventional earth drying operations. Moreover, the absence of or substantial reduction in the amount of ex-
cessively fine grains of earth makes high filtering rates possible.

Further, in our process, slurring of the hot filter cake with a sufficient quantity of the finished oil to render the mixture pumpable, permits our process to be carried out in an entirely continuous manner if finished oil filters such as Oliver continuous drum-type precoat filters are used. Slurring with naphtha at this point in the cycle would be precluded both by high temperatures and by the danger of contaminating the finished oil. Further, utilization of the efficient two tower stripping system, both for stripping the naphtha from the overheated oil and for recovering decolorized oil from the oil naphtha blend obtained from the decoking filter unit, makes the unit self contained and accomplishes the stripping in a more economical manner than if the several stripping operations or any one such stripping operation was the last mentioned washing distilling equipment. Our process also provides an efficient method for introducing new earth into the system, in that it makes provision for removing the free moisture to a sufficient extent so that when the new earth eventually meets the color solvent it will not contain sufficient moisture to harm the latter. To the extent that a naphtha is incidentally present in the earth-oil mixture supplied to the decolorizing treatment proper, the presence of naphtha, through improved contacting, promotes decolorization at relatively lower temperatures, although with efficient decolorizing earths the temperature required to effect stripping provides adequate decolorization with a time factor no longer than the minimum required for the oil to attain this temperature.

We claim:

1. The method of decolorizing a mineral oil which comprises heating a mixture including the oil, not less than about 2% and not substantially exceeding 12% of a decolorizing earth by weight on the oil, and not less than about 5% nor substantially in excess of about 65% of oil and naphtha based on the resultant blend of oil and naphtha by volume, to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil and subsequently separating the earth from the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and with naphtha from the last mentioned washing treatment to the heating treatment first mentioned.

2. The method of decolorizing a mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha to a temperature not exceeding about 480° F. but high enough to supply the heat necessary to strip the naphtha from the mixture, stripping the naphtha from the decolorized oil in the presence of the earth and subsequently the earth from the decolorized oil in a non-oxidizing atmosphere, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, and returning reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned.

3. The method of decolorizing a mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil, subsequently separating the earth from the decolorized oil, reactivating the separated earth by successive washings first with naphtha, then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, and returning reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned.

4. The method of decolorizing a mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil and subsequently filtering the earth from the decolorized oil, washing the filtered earth with naphtha to separate the retained oil and returning the resulting mixture of oil and naphtha to the heating first mentioned, subjecting the washed earth to reactivation with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil, the earth being contacted with said color solvent in the form of a slurry during said reactivation, thereafter again washing the deactivated earth with naphtha and returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned.

5. The method of decolorizing a mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil, subsequently separating the earth from the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and supplying at least a part of the naphtha obtained from the previously mentioned stripping operation to the last mentioned washing treatment.

6. The method of decolorizing mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha and traces of a color solvent to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil in two stages the second stage under lower pressure than the first, the first stage being controlled to strip a part of the naphtha and the color solvent and the second stage controlled to strip the remainder of the naphtha, and subsequently separating the earth from the decolorized oil.

7. The method of decolorizing mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha...
and traces of a color solvent to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil in two stages the second stage under lower pressure than the first, the first stage being controlled to strip a part of the naphtha and the color solvent and the second stage controlled to strip the remainder of the naphtha, subsequently separating the earth from the major portion of the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and supplying at least a part of the naphtha obtained from the first stage of the stripping operation to the last mentioned washing treatment.

8. The method of decolorizing mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha and traces of a color solvent to a temperature of from about 350° F. to about 450° F., stripping the oil solvent from the heated mixture of earth and oil in two stages the second stage under lower pressure than the first, the first stage being controlled to strip a part of the naphtha and the color solvent and the second stage controlled to strip the remainder of the naphtha, subsequently separating the earth from the major portion of the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and supplying at least a part of the naphtha obtained from the first stage of the stripping operation to the last mentioned washing treatment.

9. The method of decolorizing mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha and traces of a color solvent to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil in two stages the second stage under lower pressure than the first, the first stage being controlled to strip a part of the naphtha and the color solvent and the second stage controlled to strip the remainder of the naphtha, subsequently separating the earth from the major portion of the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and supplying at least a part of the naphtha obtained from the first stage of the stripping operation to the last mentioned washing treatment, and returning the mixture of oil and naphtha resulting from the first mentioned washing treatment to the heating treatment first mentioned.

10. A continuous method of decolorizing mineral oil which comprises passing a mixture of the oil to be decolorized and a decolorizing earth in the presence of naphtha through a heating zone and heating the mixture during its passage therethrough to a temperature of from about 350° to 450° F., stripping the naphtha from the resulting heated mixture of earth and oil, subsequently separating the earth from the major portion of the decolorized oil by filtering continuously at an elevated temperature to produce a decolorized oil filtrate and a filter cake comprising earth and retained oil, slurring the hot filter cake with a minor portion of the filtrate to produce a pumpable mixture and further slurrying the resultant mixture with naphtha, continuously passing the resulting earth-oil-naphtha slurry through a continuous decoling filter and then separating spent earth from the naphtha-oil slurry, washing the separated earth with naphtha, mixing the separated spent earth with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil the amounts of color being sufficient to cause a slurry and agitating the mixture to secure prolonged intimate contact between the color solvent and the earth, continuously supplying the last-mentioned mixture to a continuous filter and then separating reactivated earth from the color solvent and coloring matter extracted by the color solvent, washing the reactivated earth with naphtha, mixing the washed reactivated earth while still wet with naphtha with an additional quantity of naphtha sufficient to obtain a pumpable slurry, and continuously admixing the last-mentioned slurry with fresh oil to be decolorized and returning the resultant mixture to the first mentioned heating operation.

11. The method of decolorizing mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha and traces of a color solvent to a temperature of from about 350° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil in two stages the second stage under lower pressure than the first, the first stage being controlled to strip a part of the naphtha and the color solvent and the second stage controlled to strip the remainder of the naphtha, subsequently separating the earth from the major portion of the decolorized oil, reactivating the separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and supplying at least a part of the naphtha obtained from the first stage of the stripping operation to the last mentioned washing treatment, and returning the mixture of oil and naphtha resulting from the
separated earth by successive washings first with naphtha then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, returning the reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned, and returning the mixture of oil and naphtha resulting from the first mentioned washing treatment to the heating treatment first mentioned.

13. The method of decolorizing a mineral oil which comprises heating a mixture of the oil and a decolorizing earth in the presence of naphtha to a temperature of from about 400° F. to about 450° F., stripping the naphtha from the heated mixture of earth and oil, subsequently separating the earth from the decolorized oil, reactivating the separated earth by successive washings first with naphtha, then with a color solvent capable of extracting from the earth the coloring matter adsorbed from the oil and then with naphtha, the earth being contacted with the color solvent in the form of a slurry during the second mentioned washing, and returning reactivated earth wet with naphtha from the last mentioned washing treatment to the heating treatment first mentioned.

14. The method of decolorizing oil which comprises heating a mixture of the oil and reactivated decolorizing earth, in the presence of naphtha and residual color solvent more volatile than naphtha, to an elevated temperature and for a period of time adequate to effect substantial decolorization, stripping from the oil-earth mixture in succession a primary distillate containing the residual color solvent in a dry state and a secondary distillate consisting essentially of naphtha said stripping being effected while the oil-earth mixture remains at an active decolorizing temperature, subsequently separating the earth from the decolorized oil, reactivating the separated earth by subjecting it in the form of a slurry to the action of color solvent capable of extracting from the earth the coloring matter removed from the oil by said earth, washing the reactivated earth with naphtha to remove a substantial part of the color solvent retained by the earth, and returning the washed reactivated earth wet with naphtha and containing residual color solvent to the heating operation first mentioned.

ALBERT E. MILLER.
WILLIAM B. CHENAULT.
CERTIFICATE OF CORRECTION.

June 8, 1943.

WILLIAM B. CHENAULT, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 8, before the word "cils" insert --such--; page 8, first column, line 19, claim 7, for "mentioned" read --mentioned--; and second column, line 26, claim 10, after "color" insert --solvent--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of August, A. D. 1943.

Henry Van Arsdale,
(Seal)
Acting Commissioner of Patents.