UNITED STATES PATENT OFFICE.

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PURIFYING OILS.

1,277,329. Specification of Letters Patent. Patented Aug. 27, 1918.

No Drawing. Application filed March 22, 1918. Serial No. 224,038.

To all whom it may concern:

Be it known that I, ALMER McDUFFIE McAFEE, a citizen of the United States, residing at Port Arthur, in the county of Jefferson and State of Texas, have invented certain new and useful Improvements in Purifying Oils, of which the following is a specification.

This invention relates to processes of improving petroleum materials; and it comprises a method of converting relatively low grade petroleum materials into relatively higher grade materials wherein a petroleum material, such as lubricating oil, kerosene, gasolene, paraffin wax, etc., is warmed with aluminum chlorid at a relatively low temperature for a time, the temperature being below that at which aluminum chlorid will exercise any violent breaking down action upon the hydrocarbons of such material but being sufficient to permit such aluminum chlorid to exert what may be termed a saturating and stabilizing action; a temperature which, with most of these materials, is in the neighborhood of 150° F. or between 150° F. and 212° F.; the warming with the aluminum chlorid being continued until a desired degree of saturation and internal change, with corresponding improvement is accomplished; and it particularly comprises a method wherein lubricating oil, or oils of the general nature of lubricating oil, are so treated with the object of producing oils sufficiently purified to make them of higher grade for lubricating purposes or of sufficiently high grade to permit of their use for medicinal and toilet purposes; all as more fully hereinafter set forth and as claimed.

Petroleum oils and products are composed mainly or exclusively of various hydrocarbons of different boiling points. While these hydrocarbons, which are bodies consisting of hydrogen and carbon in chemical union, are very many in number and differ among themselves in chemical and physical properties, for the present purposes they may be divided into two well-known classes, the saturated hydrocarbons and the unsaturated hydrocarbons. The former are those which contain enough hydrogen to satisfy all the chemical combining power of the carbon which they also contain, while the latter are those in which the carbon has some of its affinities unsatisfied and is therefore in condition to enter into further union with oxygen and other bodies. The unsaturated hydrocarbons are presumed to owe their reactive nature to the presence of "double linkage" or "triple linkage" as the case may be; to the presence of pairs of adjacent carbon atoms united together by two or more bonds instead of union by a single bond only. The saturated hydrocarbons are relatively stable bodies; the unsaturated are relatively unstable. In all commercial petroleum products those which contain any substantial amount of unsaturated hydrocarbons are of lower grade or value than those which are free, or relatively free, of such unsaturated hydrocarbons. A lubricating oil containing any substantial amount of unsaturated oils is apt to be dark colored, or to become so on standing; and it is prone to absorb oxygen from the air with discoloration, gumming, etc. In use on a hot bearing these difficulties are of course accentuated. Like difficulties obtain in the case of gasolene, kerosene, paraffin wax and other petroleum oils and products; in all the presence of a substantial percentage of unsaturated hydrocarbons lowers their commercial grade and value. But the formation of unsaturated hydrocarbons is incidental to many of the methods in use in manufacturing petroleum products.

The unsaturated hydrocarbons occurring in petroleum oils are of course themselves oils and, except as regards the properties stated, they do not differ materially from the saturated hydrocarbons or oils which they accompany. They are hardly to be regarded as impurities; they are simply oils of less desirable character. If they be removed from the oily body, as is practicable by the use of sulfuric acid, etc., there is a resulting loss of oil.

Anhydrous aluminum chlorid ($AlCl_3$ or Al_2Cl_6) is a material capable of exercising sundry energetic reactions on the hydrocarbons which compose petroleum oil, and of modifying their character in many ways. On boiling a high-boiling petroleum oil, such as lubricating oil, a gas oil or solar oil, kerosene, etc., with aluminum chlorid, the latter, under proper conditions, will convert

the whole of such high boiling oil into lower boiling oils of the nature of gasolene, with perhaps 10 to 15 per cent. loss as gas and coke. All the distillation products of such an action will be found to be of saturated nature whatever was the nature, in this respect, of the original high boiling oil treated. By distilling a highly unsaturated gas oil, with aluminum chlorid for example, it may be converted practically wholly into gasolene and this gasolene will all be of saturated nature.

I have found that the above converting action by which high boiling oils are converted into lower boiling and the saturating action by which unsaturated oils yield saturated materials are not necessarily linked together but may be severed. And I have found that by operating at a sufficiently low temperature, instead of working at the boiling temperature just described, I can obviate the stated converting action while still retaining the saturating action. In other words, I can take a high boiling lubricating oil containing unsaturated hydrocarbons and warm it (as distinguished from heating at any high temperature) with aluminum chlorid and produce a saturation of the unsaturated constituents without production of lower boiling oils. In this action the unsaturated oils are simply transformed into saturated oils without material loss in volume or weight such as occurs in removing unsaturated compounds with sulfuric acid. This warming-up treatment with anhydrous aluminum chlorid may be applied to the improvement not only of lubricating oils but of any other petroleum product although I shall hereinafter describe it more particularly in its application to the treatment of lubricating oils. Gasolene and kerosene so treated have better burning qualities and better color; and the color does not again darken by exposure to air and light. Paraffin wax so treated does not acquire a yellow hue with age or on exposure to light. In treatment the wax is melted and then treated like an oil.

The temperatures necessary for the desired action are around 150° F. Below that temperature the saturating action becomes slower while at temperatures materially above, say at or above 212° F. there may be sufficient of the converting action to produce some low boiling oil in treating high boiling oils. With lubricating oil, kerosene, etc., any substantial production of lower boiling oils may be undesirable as unduly lowering the flash point, and with these oils it is advantageous to work at as low a temperature as is consistent with the speed of operation desired. In a general way, when working with low-boiling oils it is desirable to use a low temperature. With any oil, in a measure time and temperature are reciprocal factors; the same results can be attained at 120° F. as at 150° but somewhat more time is necessary.

In the treatment of lubricating oil with aluminum chlorid at a low temperature the unsaturated parts of the oil are saturated and the oil made much more stable against the action of air and heat. The color is also much improved. The degree to which the purification needs to be carried of course varies with the different oils and with the use which is to be made of the purified oil. In purifying any oil with aluminum chlorid, the action is more rapid at first when the proportion of unsaturated bodies is high than it is after a time when the proportion of unsaturated bodies becomes very small; and it often happens in the case of lubricating oil that carrying the purification beyond the point where the iodin number ceases to diminish rapidly is not worth while. If purification be carried to an extreme, oils are produced which are so colorless and permanent that they may be used for medicinal purposes, for internal administration, etc.

After the purification with aluminum chlorid, the oil may of course be submitted to any of the usual purifying and decolorizing treatments, with sulfuric acid, with fullers' earth, boneblack, etc. In making medicinal oil these after purifications are particularly desirable since they remove the last traces of taste and odor.

Commercial lubricating oils represent the comparatively high boiling portions of crude petroleum, from which they are prepared in appropriate ways. They range from the comparatively light and low boiling spindle oils up to heavy cylinder oils of very high boiling point. The degree to which they are ordinarily purified of course depends upon the commercial use to be made of the oil. But they are all purified more or less by elaborate treatments; and these treatments for the most part result in a loss of oil. In one method of distilling crude petroleum where the effort is to produce as large an amount as possible of gasolene, solvent oils and kerosene, distillation is pushed to this end quite irrespective of damage which may be caused to the remaining higher boiling oils. In this method of preparation the low boiling oils of the nature of gasolene and kerosene are first distilled off from the crude petroleum and then the residue in the still is subjected to a high temperature, with or without pressure, in the effort to break it up or crack it and produce a further quantity of gasolene and burning oils. The distillate so obtained is of cracked and unsaturated character and so is the residue left in the still. Lubricating oils made from such a residue are of course of highly cracked character. In other methods of operating where steam dis-

tillation is resorted to, the high boiling oils may be, and often are, also cracked to a greater or less extent. Lubricating oils made from an asphalt base stock are apt to be more injured in the various distillation treatments incident to removing lower boiling oils than are those from a paraffin base oil.

Any lubricating oil containing a substantial amount of unsaturated bodies is apt to be dark colored, unstable and show the chemical properties of the unsaturated compounds. It is not practical to thoroughly refine highly unsaturated oils to any extent with sulfuric acid for the reason that the loss of oil is too great. As lubricants, such oils in use tend to become darker colored, to gum and become tarry or resinous, and to some extent to attack metals; results due to the large amount of unsaturated compounds present. With far-going cracking in their production, these oils may be almost entirely composed of unsaturated groups.

In treating lubricating oils, or other petroleum materials, by the present process, the oil is mixed with a small amount, say 2 to 5 per cent., of anhydrous aluminum chlorid and vigorously agitated at a moderate temperature, say 150° F., for a time, with the resultant conversion of unsaturated into saturated compounds without much loss of material. It is a conversion rather than a subtraction. The action is fairly quick at first but after a time becomes slower. Its progress may be followed by testing the material from time to time with an iodin solution; the absorption of iodin by any oil being proportional to the amount of unsaturated bodies present. To obtain the same amount of improvement ordinarily requires longer with a heavy oil of the character of lubricating oil than with a lighter oil of the character of kerosene or gasolene. The oil should be dry before admixture with the aluminum chlorid and it is better to free it of sulfur compounds. Both moisture and sulfur compounds cause a waste of aluminum chlorid, and in their presence undesired reactions may occur. Vigorous agitation is necessary because the aluminum chlorid tends to settle out. The activity of the aluminum chlorid is not indefinite; after a time it loses much of its activity. After having lost some degree of its activity for the present purpose of saturating and stabilizing oils, it is still sufficiently active to be used in the production of gasolene from gas oil, kerosene, etc., at high temperatures. I therefore often use aluminum chlorid in the present process for a time and before all its catalytic activity is exhausted I remove it and use it for other purposes, replacing it by fresh aluminum chlorid. If however the aluminum chlorid is used in the present process to the exhaustion of its activity, it finally becomes converted into a coky mass containing free carbon and aluminum chlorid in what is, apparently, a bound or masked form; that is, there is apparently still anhydrous aluminum chlorid present but it no longer exhibits catalytic activity. From such exhausted material aluminum chlorid may be recovered by the process of my prior Patent 1099096. Instead of using aluminum chlorid for a time in the present process and then removing it for use elsewhere, it is of course also practical to exhaust the activity of the aluminum chlorid in a methodical way: using fresh chlorid on oil which has already been treated to some extent and after its activity is somewhat lessened, using it for treating fresh oil.

As stated, moisture is injurious to aluminum chlorid, and in using it everything must be as dry as possible to obtain its full activity and prevent undesirable reactions. If not taken directly from a still or condenser the lubricating oil is best first heated to free it of moisture. If apparatus and materials be dry, no substantial amount of hydrochloric acid is formed in the action.

In a specific embodiment employing this invention in improving lubricating oils, in a methodical way, I may take about 500 gallons of lubricating oil, which may be any of the commercial grades or a crude unpurified oil, and add to it, say, 250 pounds of anhydrous aluminum chlorid. The mixture may be warmed to about 150° F. and stirred continuously for, say, from 4 to 6 hours, the reduction in the amount of unsaturated compounds being if desired followed by testing for the iodin value. In working with any particular oil, however, the time and temperature necessary to produce the desired results are quickly ascertained and the iodin test need only be resorted to at intervals. Stirring may be stopped and the oil cooled when the iodin value is reduced as far as desired. For improving and for lubricating purposes usually a heat treatment of from two to four hours is all that is necessary, but when very highly purified oils for medicinal purposes are to be made, the time of heating may run as high as 24 hours or longer, as hereinafter described. If the treatment be carried to the total disappearance of the iodin absorption, the oil will be water-white and of perfectly stable qualities.

When the stirring is stopped and the oil becomes cool, aluminum chlorid will settle to the bottom as a blackish sludge. In the treatment of oils made from paraffin base crudes, the sludge settles quite readily and "filtering" is not difficult, but, in the treatment of oils from asphaltic base crudes, the sludge does not so readily settle, and although "filtration" with fullers' earth may

be resorted to, it is advantageous to blow dry air through the mixture of oil and aluminum chlorid to cause separation of the sludge. The sludge carries some oil in it. About 90 per cent. of the oil may be drawn off and this may be treated in the manner described; with sulfuric acid, fullers' earth, etc. To the sludge which carries about 10 per cent. of the original oil, may be added another 500 gallons of lubricating oil and the stirring and heating resumed The aluminum chlorid in the sludge still retains most of its activity. If stirring and heating are carried on until the iodin value ceases to diminish, the oil may be drawn off as a good white. The residual sludge of aluminum chlorid is less active than formerly but is capable of treating a number of further portions of oil. If a further quantity of 500 gallons be added to the sludge from this second treatment and stirring and heating resorted to until the iodin value ceases to rapidly diminish, this third portion will give an oil with considerable decolorization. Treatment of successive portions of oil may be carried on with the same portion of aluminum chlorid until a total of 3000 gallons of oil has been treated. After treating about 3000 gallons of oil with the quantity of aluminum chlorid indicated the aluminum chlorid remains incorporated in a granular coky mass from which it may be regained in any convenient manner; as by heating it in presence of a little chlorin. (Patent No. 1099096.) The aluminum chlorid volatilizes as such and may be regained.

While the operation in treating lubricating oil as just stated may be conducted as a simple treatment of a number of successive samples of oil with the same portion of aluminum chlorid, it is possible to operate in a more methodical manner; a manner in which the aluminum chlorid and the lubricating oil, so to speak, travel in "countercurrent." For example, fresh crude lubricating oil may be treated with aluminum chlorid which has served for several other portions of oil and is nearly exhausted as to its activity. The oil so treated may then be stirred up several times with as many portions of aluminum chlorid which have been previously used, until the nearly purified oil is finally treated with fresh aluminum chlorid. For example, aluminum chlorid which has treated five previous quantities of oil may be brought into contact with fresh lubricating oil. The lubricating oil drawn off from this portion of aluminum chlorid is next treated with aluminum chlorid which has been used on four previous samples of oil; the oil thus treated is next treated with aluminum chlorid which has been used on three previous samples and so on. In operating in this methodical way, the time of contact between each portion of oil and of aluminum chlorid need not be so long as in the previously described alternative method. The progress of the reaction can be followed with iodin as before.

While I have described the operation as used in a series of vessels, it is obvious that by suitable mechanical appliances, the oil and aluminum chlorid may be methodically brought into reaction in other ways. One convenient way is: arrange a series of, say, six vessels each provided with stirring devices, in such a manner that oil may be caused to flow through the series in any desired way; the pipe connections for this purpose being much like those in the ordinary "diffusion battery" used for sugar extraction; that is, so that each vessel can be made in its turn first, last and the intermediate members of the series, as regards the flowing current of oil. The use of conveyers, etc., for physically moving aluminum chlorid against the current of oil is less convenient. After each treatment with the chlorid the liquid should be allowed to cool to promote deposition.

At the treating temperature, the aluminum chlorid dissolves extensively in the oil, but the dissolved chlorid comes out again on cooling to ordinary temperature.

As stated, it is advantageous that all the oils and materials used be dry as any moisture present wastes aluminum chlorid. With dry materials, ordinary steel or iron vessels and connections may be used. Copper and lead lined vessels may be used but are not necessary. Pottery or stoneware vessels may be used but are more expensive than iron.

The present process may be applied to acid-treated commercial oils but it is better used with untreated oils, thereby producing an economy of acid.

The lubricating oil treated may be that coming from any crude oil whether paraffin base or asphalt base or naphthenic in character. Extensively cracked oils undesirable with other methods of refining are readily and effectually treated by the present method. Lubricating oils made from the Texas asphaltic crudes are readily and advantageously treated. Such oils are apt to exhibit a relatively high iodin number, corresponding to a high degree of unsaturation. By treating them with aluminum chlorid in the manner described the iodin number tends to disappear and the color and stability are improved.

The present process may be used on sulfur containig lubricating oils but is better adapted to those free of, or low in, sulfur as the presence of sulfur impairs the period of activity of the aluminum chlorid.

In lieu of aluminum chlorid other catalytically acting chemicals capable of produc-

ing an internal condensation with deposition of carbon and saturation of unsaturated groups may be used. Other metallic halids, such as zinc chlorid and ferric chlorid tend to produce the same results but with most oils are not as active as aluminum chlorid. Titanium chlorid, antimony trichlorid, etc., may also be used.

In making medicinal oil I proceed substantially as above stated, but I ordinarily carry on the operation for some time after the rapid diminution in the iodin number stops. With many oils the iodin number will cease to diminish rapidly after about 2 to 6 hours' treatment while with others there may be a progressive diminution of the iodin number for as long as 24 hours. This is particularly the case with oils derived from an asphaltic base crude petroleum. But in any event I find that to produce a medicinal oil, warming with aluminum chlorid to a temperature around 150° F should be for a relatively long time; usually around 24 hours. The time necessary of course depends on the character of the oil, on the nature of the purifying steps which follow the aluminum chlorid treatment and other conditions, and at times good results may be obtained with a less period of warming, even as low 6 to 8 hours, but as a rule 20 to 24 hours' warming is advantageous. In securing the high purity necessary for these oils I ordinarily employ more aluminum chlorid than where the object is merely to improve a lubricating oil and raise its commercial grade as a lubricating oil. I may, for instance, employ about 10 to 12 per cent. of aluminum chlorid calculated on the weight of the oil under treatment; say, a pound to a gallon, although the exact quantity will depend, of course, upon the particular characteristics of the particular oil under treatment. I find it better to use naphthene-rich oils derived from petroleums having an asphaltic or semi-asphaltic base, such as the Texas oils, or certain naphthenic California oils.

After completion of the aluminum chlorid reaction, the oil is submitted to certain further purifying operations. Most of the aluminum chlorid, but not all, will settle out as a sludge on cooling the mixture and that which remains in suspension and solution must be removed. The oil at this stage is not decolorized but on the other hand is usually blackish or reddish in color from the presence of dissolved and suspended aluminum chlorid compounds. It also has a strong taste, is not odorless and usually indeed has an odor of sulfuretted hydrogen. This oil I next treat with sulfuric acid, which is used mainly for the purpose of removing the remaining aluminum chlorid. No water should be allowed to come in contact with the oil after the aluminum chlorid treatment and before the acid treatment. The acid treatment may be usefully repeated and particularly in the case of oils which tend to display a fluorescence or "bloom." One or two per cent. by volume of sulfuric acid will suffice. If bloom is also to be removed, the quantity of acid may be increased somewhat. Fuming sulfuric acid of any commercial strength may be employed; or the ordinary oil of vitriol may be used. After the acid treatment, ample time should be allowed for settling and depositing the compounds formed by the acid.

The settled and clarified oil is next given an alkali wash in order to neutralize and remove any dissolved sulfuric acid compounds from the oil; that is, the oil is agitated with a solution of any suitable alkali, such as a solution of caustic soda. It is then washed with water to remove the excess alkali.

The remaining taste and odor are removed with super-heated steam which carries away some hydrocarbons of the kerosene series having taste and odor and renders the oil completely tasteless and odorless. Since the steaming may leave the oil sufficiently moist to cloud on cooling the oil may be next dried. This may be effected by blowing air through it for a time while it is still warm. Finally the oil is filtered and freed of mechanical impurities, advantageously with fullers' earth or other pulverulent decolorizing filtered material, such as bone-black. This filtration with decolorants has the advantage that any remaining color is removed.

The product made in the stated manner is colorless, tasteless, odorless and has a flash point of not below 325° F., and a boiling point as high as 650° F. or above. It is substantially inert to all ordinary chemical reagents and responds to the most stringent tests of the various pharmacopœias for hydrocarbon oils for internal or external use. Because of its neutral permanent characteristics it may be used as a basis for the manufacture of perfumes; as in the well known enfleurage process.

The sludge resulting from the above process may be added to fresh lubricating oil as has been above described or it may be used in making gasolene from gas oil, solar oil, etc., in accordance with the process of my application Serial No. 792,615, filed September 30, 1913. A more advantageous application of this partly exhausted sludge and one which is more particularly contemplated in the present invention, is its use for making the original material for the manufacture of medicinal oils. For this purpose crude petroleum oil may be freed of low boiling constituents, if any substantial amount be present, and then admixed with

the sludge and the mixture boiled in such a manner as to convert part but not all of the oil into low boiling oils, such as gasolene. The oil remaining in the still after the removal of this low boiling fraction is particularly suitable as a source of material for making medicinal oils since it has been purified and internally changed in this boiling operation. For one thing it is freed of much of its sulfur. I do not herein claim the process of improving oils by heating a high boiling oil with aluminum chlorid while distilling off low boiling oils formed thereby and thus improving the residual oil in the still, as such a process forms the subject of my Patent No. 1,127,465, granted February 9, 1915. However the residual oil of the said patented process is particularly applicable for use in making medicinal oil, if it be subjected to further warming with aluminum chlorid as has been described and to the acid, alkali, steaming and air treatments.

After the treatment just described, the oil from which the aluminum chlorid has been settled out may be used as a whole for making my medicinal oil. For this purpose it may be treated with a little sulfuric acid, neutralized, washed and dried and then warmed as previously described with fresh aluminum chlorid. But it is better to redistil it using live or "bottom" steam and take a fraction of the distillate for making medicinal oil. The fraction having a viscosity of say 185 to 250 on the Saybolt universal viscosimeter, with a 300 to 325 flash point is well adapted. When this special distillate is taken off, the residue remaining in the still will have the general characteristics of cylinder stock.

The special distillate just described is next dried. This may may be done by heating it to 150° F. and blowing air through for a time. To the warm dry oil at this temperature is next added a rather large proportion of fresh, highly active aluminum chlorid; say a pound to the gallon or 42 pounds to the barrel. The same proportion of chlorid may be used when the whole body of residual oil is taken instead of the selected distillate. The oil and aluminum chlorid are maintained in contact with energetic stirring at a temperature around 150° F. for such a time as may be necessary. Generally I maintain the contact 20 to 24 hours. The iodin value may cease to rapidly diminish, becoming reduced to a negligible quantity, at the end of 4 to 6 hours. At the end of the chlorid treatment the warm oil is allowed to cool to the ordinary temperature whereupon the greater part of the aluminum chlorid settles out as a sludgy mass; the material hereinbefore referred to as once-used aluminum chlorid sludge. Any dissolved or suspended aluminum chlorid which may remain in the oil may now be removed as already described. The oil may be treated with sulfuric acid to remove the chlorid. After the sulfuric acid treatment the oil is given a neutralization with alkali, washed with water, and steamed by the introduction of superheated steam. It is advisable to continue this steaming, using plenty of steam heated to a temperature of, say, 500–600° F., until a sample of the oil becomes absolutely tasteless. The oil is next filtered through or contacted with fullers' earth and is ready for packaging or sale.

For the warming operation any ordinary water jacketed kettle, or the like, provided with stirring means may be used. Water is better adapted to maintaining a low temperature such as 150° F. than is steam.

This application is a consolidation in part of my prior applications Serial Numbers 792,617, filed September 30, 1913; 875,532, filed December 4, 1914, and 65,289, filed December 6, 1915.

What I claim is:—

1. The process of improving petroleum materials, which comprises warming such a petroleum material with a catalytic metallic halid at a temperature around 150° F.

2. The process of improving petroleum materials, which comprises warming such a petroleum material with aluminum chlorid at a temperature around 150° F.

3. The process of improving petroleum materials, which comprises a treatment thereof with anhydrous aluminum chlorid at a temperature and for a time sufficient to produce a substantial degree of saturation of unsaturated groups in the material, but insufficient to produce any substantial lowering of the boiling point of such petroleum material.

4. The process of improving petroleum products containing unsaturated hydrocarbons, comprising the warming of such a product in the presence of anhydrous aluminum chlorid until the unsaturated hydrocarbons are transformed into saturated bodies to a substantial extent but without material reduction in the original boiling point of such product.

5. The process of decolorizing, stabilizing and deodorizing petroleum materials, which comprises warming such a material with anhydrous aluminum chlorid for a time and at a temperature sufficient to produce these results, while insufficient to cause a conversion of the original oil components of such material into lighter oils to any substantial degree.

6. The process of improving petroleum materials containing unsaturated hydrocarbons, which comprises warming such petroleum material with anhydrous aluminum chlorid at a temperature below that at which the identity of such material will be sub-

stantially changed and continuing the warming till a substantial proportion of such unsaturated hydrocarbons are transformed into saturated hydrocarbons.

7. The process of stabilizing, decolorizing and deodorizing petroleum oils containing unsaturated oils, which comprises warming such an oil with anhydrous aluminum chlorid at a temperature sufficient to transform such unsaturated oils into saturated oils while insufficient to cause a substantial lowering of the original flash point of such petroleum oil.

8. In the purification of high boiling mineral lubricating oils the process which comprises warming such an oil with dry aluminum chlorid at a temperature insufficient to volatilize any substantial proportion of the oil under treatment.

9. In the purification of high boiling mineral lubricating oils, the process which comprises heating such oil with dry aluminum chlorid to a temperature around 150° F.

10. In the purification of high boiling mineral lubricating oils, the process which comprises heating such oil with dry aluminum chlorid to a temperature around 150° F., allowing the oil to cool and separating the oil from the chlorid sludge.

11. In the purification of high boiling mineral lubricating oils, the process which comprises heating such oils with dry aluminum chlorid to a temperature around 150° F., allowing the oil to cool, separating the oil from the chlorid sludge and heating such sludge with a fresh portion of oil.

12. In the purification of high boiling mineral lubricating oils, the process which comprises heating such oil with dry aluminum chlorid to a temperature around 150° F., allowing the oil to cool, separating the oil from the chlorid sludge and heating such sludge with a fresh portion of oil, these operations being repeated until the sludge separated becomes a granular coky mass.

13. In the purification of high boiling mineral lubricating oils, the process which comprises warming dry aluminum chlorid with a plurality of portions of such oil and such portions of oil with a plurality of portions of aluminum chlorid, the operation being so conducted that fresh oil is first contacted with nearly exhausted chlorid and nearly purified oil is finally treated with fresh chlorid.

14. The process of bleaching, stabilizing and purifying lubricating oils which comprises producing an internal condensation attended with deposition of carbon and saturation of unsaturated groups by warming such oil with a catalytic chemical and thereafter treating with a pulverulent decolorizer.

15. The process of making medicinal oils which comprises warming a high boiling oil with a catalytic metallic halid for a period of time at a temperature insufficient to form any substantial amount of volatile oils, removing the catalytic halid and treating the oil with sulfuric acid, and steaming until taste is removed.

16. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid for a prolonged period of time at a temperature insufficient to make volatile oils, removing the aluminum chlorid and treating with sulfuric acid, and steaming till taste is removed.

17. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid for a prolonged period of time at a temperature insufficient to make volatile oils, removing the aluminum chlorid, treating with sulfuric acid, steaming till taste is removed and finally filtering through a decolorant.

18. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid to a temperature of about 150° F. for a prolonged period of time, removing the aluminum chlorid and treating with sulfuric acid, and steaming till taste is removed.

19. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid to a temperature of about 150° F. for a prolonged period of time, removing the aluminum chlorid and treating with sulfuric acid, steaming till taste is removed, and finally filtering through a decolorant.

20. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid for about 24 hours at a temperature insufficient to make volatile oils, removing the aluminum chlorid and treating with sulfuric acid, and steaming till taste is removed.

21. The process of making medicinal oils which comprises warming a high boiling oil with aluminum chlorid at a temperature insufficient to make volatile oils till the iodin number ceases to diminish, removing the aluminum chlorid and treating with sulfuric acid, and steaming till taste is removed.

22. The process of making medicinal oils which comprises warming with aluminum chlorid a high boiling petroleum oil derived from a crude petroleum having an asphaltic base, such warming being for a prolonged period of time and at temperature insufficient to make volatile oils, removing the aluminum chlorid and treating with sulfuric acid, and steaming till taste is removed.

23. The process of making medicinal oils which comprises warming with aluminum chlorid a high boiling petroleum oil derived from a crude petroleum having an asphaltic base, such warming being for a prolonged

period of time and at a temperature insufficient to make volatile oils, removing the aluminum chlorid and treating with sulfuric acid, steaming till taste is removed, and finally filtering through a decolorant.

24. The process of making medicinal oils which comprises boiling an oil with aluminum chlorid for a time and thereafter warming oil so treated with fresh aluminum chlorid at a temperature insufficient to make volatile oils.

25. The process of making medicinal oils which comprises boiling an oil with aluminum chlorid for a time, removing the chlorid from the residual high boiling oil, separating such residual oil into two portions by distillation and thereafter warming one such portion with fresh aluminum chlorid at a temperature insufficient to make volatile oils.

26. The process of making medicinal oils which comprises boiling an oil with once-used aluminum chlorid for a time and warming oil so treated with fresh aluminum chlorid at a temperature insufficient to make volatile oils.

27. In the manufacture of medicinal oils, the process which comprises boiling an asphaltic crude oil with once-used aluminum chlorid from a later operation till a portion but not all of said oil is removed as low boiling products, removing the aluminum chlorid, warming oil which has been so treated with fresh aluminum chlorid at a temperature insufficient to make volatile oils to purify such oil and furnish such once-used chlorid, removing the chlorid, treating with sulfuric acid, and washing, steaming the oil and filtering through a decolorant.

28. In the manufacture of medicinal oils, the process which comprises boiling an asphaltic crude oil containing naphthenes with once-used aluminum chlorid from a later operation till a portion but not all of said oil is removed as low boiling products, removing the aluminum chlorid, warming a distilled fraction of the oil which has been so treated with fresh aluminum chlorid at a temperature insufficient to make volatile oils to purify such oil and furnish such once-used chlorid, removing the chlorid, treating with sulfuric acid, washing, and steaming the oil and filtering through a decolorant.

29. In the purification, stabilization and decolorization of petroleum oils the process which comprises warming such oil at a temperature insufficient to volatilize substantial amounts of the oils with 2 to 10 per cent. of anhydrous aluminum chlorid until rapid diminution of the iodin number ceases.

In testimony whereof I have hereunto affixed my name this 19th day of March, 1918.

ALMER McDUFFIE McAFEE.