UNITED STATES PATENT OFFICE.

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ART OF PURIFYING PETROLEUM, AND IN PRODUCTS THEREFROM.

SPECIFICATION forming part of Letters Patent No. 649,047, dated May 8, 1900.

Application filed November 1, 1888. Serial No. 289,747. (No specimens.)

To all whom it may concern:

Be it known that I, HERMAN FRASCH, of Cleveland, in the county of Cuyahoga and State of Ohio, have invented a new and useful Improvement in the Art of Purifying Petroleum, and in Products Therefrom; and I do hereby declare the following to be a full, clear, and exact description thereof.

This invention has reference to the manufacture of certain new or improved products of the kind known as "reduced oils" and employed for lubricating machinery from that class of petroleums distinguished by the presence of a large proportion of sulfur compounds which resist the ordinary treatment for the removal of sulfur and which render the oil unfit for general use on account of their very disgusting odor. These petroleums contain sulfur in large quantities, usually over one-half of one per centum, and being found in Canada and at Lima, in the State of Ohio, are generally known as "Canadian" oil or "Lima" oil. The malodorous compounds therein have received the suggestive name of "skunk" among the workmen in this class of petroleums.

In a prior patent, No. 378,246, dated February 21, 1888, and in prior applications I have described and claimed processes for obtaining certain purified products from the skunk-bearing Lima or Canadian oil; but such processes involve the distillation of the products whose purification is to be obtained and are therefore unsuited to the manufacture of reduced-oil products, which consist, substantially, of the heavier constituents of the crude petroleums in their natural state, except for the removal of the lighter hydrocarbons, and which cannot be distilled without destroying their special fitness for lubricating purposes. Moreover, before any of my said inventions it had been customary in Canadian refineries and in some refineries in the United States to take malodorous skunk-containing burning-oil distillates which had been treated with sulfuric acid and washed with water and to treat the same with an aqueous solution of plumbate of soda in order to effect deodorization and then to add powdered sulfur in order to restore the color and to cause the quick precipitation of the lead, the soda solution then settling gradually to the bottom. This treatment is also unsuitable for the production of reduced-oil products, both because of the disadvantages and alterations in the hydrocarbons which attend the preliminary treatment with sulfuric acid, as well as on account of the preceding distillation of the products.

It has long been recognized that the heavier portions of petroleums—that is to say, the portions of the crude oil which remain after the elimination of the burning-oil fraction and of so much of the next-heavier fraction as may be desired and which have a gravity of about 29° Baumé (the range being a few degrees on each side of this number, but for the most part under rather than above the same)—are in general especially well suited to purposes of lubrication in their natural state and that to utilize these natural lubricating properties not only must the heavier hydrocarbons be themselves substantially unaltered, (whether by acid treatment or by distillation,) but they must be reasonably free (the freer the better) from "cracked" products, and especially from solid carbon, "cracking" being apt to set free in the residuum microscopic particles, or from other solid particles which would injure the lubricating quality of the oil.

The heavier portions of Canadian or Lima oil are of good lubricating quality in their natural state; but they are not useful in this condition on account of the malodorous nature of the peculiar sulfur compounds which exist in the crude oil.

In accordance with the present invention the heavier portions of Canadian or Lima oil freed from the burning-oil fraction and of a gravity of about 29° Baumé—reduced oils, in other words, from Canadian or Lima petroleums—are obtained in a fair-smelling condition, while still possessing in as great or even greater degree the good lubricating quality of the natural constituents of these oils.

My said invention is based principally upon the discovery made by me that the peculiar sulfur compounds in the reduced Canadian or Lima oils impart to such oils the property of dissolving lead oxid and certain other metallic oxids, with the result of forming hydro-

carbon - sulfur - oxygen - metal compounds which are inodorous in comparison with the natural malodorous hydrocarbon-sulfur compounds and that this transformation in the skunk can be effected without deteriorating the natural lubricating constituents of the oil. By so converting all the malodorous compounds in the reduced oils every objection to their use as lubricants is removed, notwithstanding the continued existence of the now inodorous skunk therein. The presence of these inodorous compounds of skunk with oxygen and metal, or, in other words, the inodorous hydrocarbon - sulfur - oxygen - metal compounds, is, in fact, believed to be advantageous in improving the lubricating qualities of the oils, the improvement being more particularly attributed to the metal forming part of the compounds which remain in solution in the oils and associated therewith in a special manner. The metal is not, however, essential to the inodorous character of the new skunk compounds, for the metal may be precipitated from any of the reduced oils by the addition of sulfur or otherwise, leaving the reduced oil inodorous and also possessed of its natural lubricating quality, but of course without the benefit of any increase of lubricating capacity, due to metal forming part of the dissolved compounds. Moreover, by other suitable oxidating agents a similar deodorization may be effected without impairment of the natural lubricating quality, hydrocarbon - sulfur - oxygen compounds free from metal being obtained and remaining dissolved in the oil.

My invention therefore consists in the new or improved process or processes of making reduced-oil products from the skunk-bearing Lima or Canadian petroleums by uniting oxygen, with or without metal, to the malodorous hydrocarbon-sulfur compounds, so as to form therefrom inodorous bodies containing hydrocarbon sulfur and oxygen, with or without metal, by means of reagents which are without chemical effect upon the hydrocarbons in which the skunk is dissolved, and therefore do not deteriorate the principal lubricating constituents of said oils and which most advantageously consist of one or more metallic oxids soluble in the malodorous skunk-bearing oil.

My invention also consists in the new or improved fair-smelling reduced-oil products from Lima or Canadian petroleums.

In carrying out this invention with soluble metallic oxid it is considered most advantageous to reduce the malodorous crude Lima or Canadian oil to the gravity desired (which would generally be about 26° or 27° Baumé when about half of the crude oil has been evaporated) before dissolving the metallic oxid therein. This is considered more advantageous than to attempt to reduce crude oil having the metallic oxid dissolved therein, because if metallic oxid is dissolved in the crude oil before reduction the vaporization of the lighter hydrocarbons with a portion of the skunk results in a decomposition of the previously-formed hydrocarbon - sulfur-oxygen-metal compounds and the precipitation of an insoluble metallic sulfid, and this precipitate would have to be removed from the reduced oil, thus adding to the expense of manufacture and creating a danger of injury to the quality of the product by the presence therein of solid particles which might escape removal. The presence of the foreign matters in the oil during reduction also makes it more difficult to avoid cracking, which may easily proceed so far that the residuum would not belong in the same class with reduced oils, even if filtered or otherwise treated for removal of the cracked products. Moreover, the malodorous skunk appears again in the liquid oil as the before-mentioned decomposition and precipitation proceed unless metallic oxid is constantly present to combine with it as it forms again. It is possible, however, and not outside the limits of the invention to combine oxygen and metal with the skunk in the reduced oil in the reducing operation by evaporating the lighter products from the crude oil while soluble metallic oxid is present in the oil undergoing reduction, resort being had when necessary to a further deodorization after reduction. The soluble metallic oxid can be dissolved in the malodorous reduced oils (or in the malodorous crude oils) of the Canadian or Lima class without the aid of any added reagent; but it expedites the solution to employ, in connection with said oxids, a fatty or resinous acid—such as oleic, stearic, or colophonic acid—and its employment in this connection constitutes a special improvement. It is generally useful for expediting the solution of soluble metallic oxid in skunk-bearing oils, as well in distillate oils as in undistilled, and may be employed in any case where such solution is to be effected. So far as I am aware it was never before used for any such purpose, and the improvement involving its use is intended to be secured generally for all the uses to which it may be applicable, as well as more particularly for the manufacture of reduced oil products.

In the manufacture of my new or improved reduced-oil products by what is considered the best mode of working I subject the crude Canadian or Lima oil to the distilling operation technically known as "reduction," in which, as is well known, the lighter parts of the oil, consisting of the gasolene, naphtha, and burning-oil fractions, with so much as may be desired of the next-heavier fraction, are removed without alteration of the heavier undistilled portions further than results necessarily from such removal, for cracking and overheating are carefully avoided. In this operation the oil is reduced to the desired gravity, about fifty per centum of the original crude oil being generally distilled off and the gravity of the reduced oil in consequence reaching about

26° or 27° Baumé. To about one hundred barrels of the malodorous reduced oil thus produced without previous treatment with sulfuric acid or other reagent which would injure the lubricating constituents of the oil I add two hundred pounds of oxid of lead (litharge) and five hundred pounds of a fatty or resinous acid—as stearic, oleic, or colophonic acid, for example—and I heat this mixture of reduced oil, lead oxid, and fatty or resinous acid in a closed vessel or digester to a temperature of about 400° Fahrenheit, the said mixture being subjected to constant agitation by means of a suitable mechanical agitator. The agitation is kept up for, say, eight or ten hours, until a sample on withdrawal shows that it has been fully deodorized. The agitation keeps the undissolved solid matter in suspension and aids in the solution thereof. When deodorization is complete, the agitation is stopped and the digester is allowed to cool. Any undissolved oxid may be separated by settling, and after settling the supernatant oil is drawn off ready for use. When the operations have been carefully conducted, the oil contains the skunk in the form of inodorous hydrocarbon-sulfur-oxygen-metal compounds, is free from cracked products, especially the fine particles of solid carbon, and has the lubricating qualities of the heavier portions of the crude oil in their natural state, together with such further lubricating capacity as may be due to the newly-formed skunk compounds.

The proportion of lead oxid and fatty or resinous acid (either or both) may be varied, and the acid may be omitted, since the oxid is directly soluble in the skunk-bearing oil. When the fatty or resinous acid is used, it remains in the reduced oil. When it is not used, the digestion will have to be carried on longer, since the effect of such acid is to facilitate and hasten the solution of the metallic oxid or, as it may be otherwise expressed, the formation of the inodorous hydrocarbon-sulfur-oxygen-metal compounds.

The degree of heat which I have named as the proper temperature to which the mixture should be raised may be varied, a greater or less degree being employed. A temperature of 400° Fahrenheit is, however, as high as reduced oil can conveniently be heated, and less temperatures are not so good, because the less the temperature of the mixture the longer must the agitation thereof be continued to effect perfect deodorization. The use of the closed vessel for containing the oil during its treatment is desirable, because it not only prevents vaporization of the oil, but by excluding the air it prevents it from so oxidizing the oil as to make it tarry in appearance.

Instead of treating the reduced oil in a close vessel with agitation other suitable apparatus may be used. For example, I may charge a filter with a mixture of lead oxid and some other substance to act as a carrier, such as plaster-of-paris, so that a bed permeable to the oil will be formed, and I may pass the malodorous reduced oil through the so-charged filter when heated, the said oil being preferably mixed first with a fatty or resinous acid, as above set forth. This mode of practicing my invention is feasible, but it is subject to objection on account of the large number of filters which would be required and also because of the slowness of this way of effecting deodorization.

If it should be desired so to do, metallic oxid, (litharge, for example,) with or without a fatty or resinous acid, may be added in whole or in part to the oil during or before reduction, and when the desired gravity is reached the so-reduced oil holding in solution a portion of said oxid or, as it may otherwise be expressed, holding in solution the hydrocarbon-sulfur-oxygen-metal compounds which have been formed by the union of the said oxid with the skunk may be separated from the precipitate of metallic sulfid and when necessary be further treated with the lead oxid, with or without an addition of fatty or resinous acid. If a sufficient proportion of metallic oxid (which proportion should be much larger than that given above) is present in the oil during reduction, the deodorization of the reduced oil may be complete at the end of the reducing operation, so that no further operation for that purpose would then be necessary; but if the proportion of oxid is insufficient or if for another reason the undistilled residual oil is not sufficiently deodorized it should receive further treatment for deodorization, as above set forth. In any case, however, this procedure is objectionable on account of the presence of the sulfid precipitate in the reduced oil (which must be removed) and also because it is more difficult to carry on the reduction without cracking if the oxid and other foreign matters are then present in the oil.

After the deodorization of the reduced oil by combining the skunk (after or during reduction) with metallic oxid, so as to form inodorous hydrocarbon-sulfur-oxygen-metal compounds, as above set forth, the metal may be precipitated by suitable means—such, for example, as an addition of sulfur in powder—leaving the skunk still in the inodorous oxidated condition without alteration of the lubricating qualities further than these may be changed by the removal of the metal; but, as already said, it is preferable to leave the metal in the combination.

Instead of the whole or a portion of the lead oxid one or more of the other metallic oxids soluble in skunk-bearing oil may be used. They are oxids of metals of the class which is precipitable in acid solution by hydrogen sulfid. The oxids of bismuth, cadmium, mercury, copper, and silver may be mentioned. Lead oxid is considered best, however, on account of its cheapness and ready solubility.

Instead of using the soluble oxids in their

own proper form they may be used in the form of their readily decomposable or soluble compounds, such as the carbonates, fatty or resinous salts, manganates, chlorates, and like salts of the metals mentioned. The plumbate of soda is a compound of lead oxid which may be used—as, for example, by treating the reduced oil with an aqueous solution of this compound formed by dissolving lead oxid (litharge) in an aqueous solution of caustic soda; but such treatment is objectionable by introducing water and alkali, which have a tendency to emulsify the oil.

Instead of using soluble metallic oxids (simple or in the form of decomposable or soluble compounds) any suitable oxidating agents may be used—that is to say, oxidants which are without chemical effect under the conditions of working upon the hydrocarbons in which the skunk is dissolved, the oxidation converting this latter hydrocarbon-sulfur-oxygen compound. Such an oxidant is the binoxid of manganese, which may be agitated with the reduced oil in a close vessel at 400° Fahrenheit or at a greater or less temperature, as described above for lead oxid, until a sample shows that the deodorization has been effected. The so-deodorized reduced oil when separated from the solid residue of the lower oxids of manganese and of any undecomposed binoxid is ready for use.

In applying the process of my before-mentioned patent to crude petroleum the distillation therein prescribed involved, incidentally, the heating of said crude petroleum with the oxidating oxids in the still; but in that case no precautions were indicated to be taken to avoid such temperature and other conditions as would cause a cracking of the hydrocarbons and a consequent production of carbon particles or of other bodies which would render the residuum of the said crude oil incapable of entering the class of reduced oil. The production of any oil of this class would be unlooked for, and, indeed, no production of a residual product which should serve as a lubricant was contemplated or would be obtained without the employment of more than is set forth in said patent.

In order to avoid repetition in the following claims, I wish it to be understood that the term "metallic oxid" as used therein is intended to include any one or more of the metallic oxids soluble in skunk-bearing petroleum and their decomposable or soluble compounds.

I claim herein as my invention or discovery—

1. The process of making from Lima or Canadian petroleums, which contain the sulfur compounds termed "skunk," fair-smelling reduced-oil products for lubricating purposes, consisting in reducing the skunk-bearing crude petroleum to a gravity of about 29° Baumé by evaporating the burning-oil and other lighter portions at such temperatures and under such other conditions as to avoid the liberation of microscopic particles of carbon or other decomposition which would exclude the said residual product from the reduced-oil class, and in subjecting the undistilled heavier portions of said skunk-bearing petroleum in their natural state to oxidants which are without effect upon the hydrocarbons wherein the skunk is dissolved, so as to convert the skunk therein into inodorous oxidized compounds while preserving the lubricating quality of the said undistilled heavier portions of the crude petroleum, the addition of oxidant being before or after the evaporation of the said lighter portions, substantially as described.

2. The process of making from Lima or Canadian petroleums, which contain the sulfur compounds termed "skunk," fair-smelling reduced-oil products for lubricating purposes, consisting in reducing the skunk-bearing crude petroleum to a gravity of about 29° Baumé by evaporating the burning-oil and other lighter portions at such temperatures and under such other conditions as to avoid the liberation of microscopic particles of carbon or other decomposition which would exclude the said residual product from the reduced-oil class, and in dissolving metallic oxid in the undistilled heavier portions of said skunk-bearing petroleum in their natural state so as to convert the skunk therein into inodorous oxidized compounds while preserving the lubricating quality of the said undistilled heavier portions of the crude petroleum, the metal in said compounds being useful for lubrication if allowed to remain but being precipitable therefrom without formation again of the malodorous skunk should it be desired to remove such metal, substantially as described.

3. The process of making from Lima or Canadian petroleums, which contain the sulfur compounds termed "skunk," fair-smelling reduced-oil products for lubricating purposes, consisting in reducing the skunk-bearing crude petroleum to a gravity of about 29° Baumé by evaporating the burning-oil and other lighter portions at such temperatures and under such other conditions as to avoid the liberation of microscopic particles of carbon or other decomposition which would exclude the said residual product from the reduced-oil class, and in subjecting the undistilled heavier portions of said skunk-bearing petroleum in their natural state, in a close vessel at a temperature above the boiling-point of water but below the distilling-point of said heavier portions of the oil and most advantageously at about 400° Fahrenheit, to agitation with metallic oxid in sufficient quantity to convert all the skunk into inodorous oxidized compounds, and when there is precipitated or other solid matter in the so-deodorized reduced-oil product separating it therefrom, substantially as described.

4. The process of making from Lima or Canadian petroleums, which contain the sul-

fur compounds termed "skunk," fair-smelling reduced-oil products for lubricating purposes, consisting in reducing the skunk-bearing crude petroleum to a gravity of about 29° Baumé by evaporating the burning-oil and other lighter portions in the absence of metallic oxid at such temperatures and under such conditions as to avoid the liberation of microscopic particles of carbon or other decomposition which would exclude the said residual product from the reduced-oil class, and in dissolving metallic oxid in the malodorous undistilled skunk-bearing residuum of such evaporation, so as to convert the skunk therein into inodorous oxidized compounds while preserving the lubricating quality of the said undistilled heavier portions of the crude petroleum, the reduction in the absence of metallic oxid avoiding the precipitation of metallic sulfid in the residuum which would occur if the metallic oxid were dissolved in the petroleum before the reduction thereof, substantially as described.

5. The improvement in the deodorization of skunk-bearing petroleums, consisting in dissolving in the oil under treatment together with metallic oxid a fatty or resinous acid or acids, to facilitate and expedite the solution of the oxid in the oil, the oil being withdrawn for use or sale with the deodorized skunk therein, substantially as described.

6. A fair-smelling reduced-oil product for lubricating purposes, composed of the heavier undistilled portions of the skunk-bearing Lima or Canadian crude oil, free from the burning-oil fraction and of about 29° Baumé gravity, with the skunk therein in the form of inodorous hydrocarbon-sulfur-oxygen compounds, and with the principal lubricating constituents of said oil in their natural state, the said product being free from residues of cracking, especially the fine particles of solid carbon, substantially as described.

7. A fair-smelling reduced-oil product for lubricating purposes, composed of the heavier undistilled portions of the skunk-bearing Lima or Canadian crude oil, free from the burning-oil fraction and of about 29° Baumé gravity, with the skunk retained therein in the form of inodorous hydrocarbon-sulfur-oxygen compounds, having metal united to the hydrocarbon, sulfur and oxygen of said compounds and thus retained in solution in said product, so as to improve its lubricating quality, said product having the natural constituents of said crude oil unimpaired as to their lubricating properties and being free from residues of cracking, especially the fine particles of solid carbon, substantially as described.

In testimony whereof I have hereunto set my hand this 11th day of October, A. D. 1888.

HERMAN FRASCH.

Witnesses:
W. B. CORWIN,
J. K. SMITH.