Patented May 9, 1933 1,908,646

# UNITED STATES PATENT OFFICE

IGNAZ ROSENBERG, OF BERLIN, GERMANY, ASSIGNOR TO THE FIRM "EDELEANU" GESELLSCHAFT M. BESCHRÄNKTER HAFTUNG

## TREATMENT OF MINERAL OILS WITH LIQUID SULPHUR DIOXIDE

No Drawing. Application filed August 8, 1929, Serial No. 384,460, and in Germany June 26, 1928.

The Edeleanu process as described in Patent No. 911,553 has hitherto been applied in practice only for the refining of certain clean cut fractions of petroleum oil, and particularly the illuminating oil and lubricating oil fractions. In certain cases the benzine fraction has also been subjected to the Edeleanu process, generally, however, for the purpose of facilitating the isolation from the extract obtained of the benzene and toluene present in the benzine. The subjection of the total distillate of the mineral oil as such, without previous fractionation into benzine, illuminating oil, gas oil, heating oil and lubricating oil, to the Edeleanu process has hitherto been avoided because in using the process there would be subjected to the refining the fractions which it was believed were not commercially worthy of separation into saturated and unsaturated hydrocarbons.

Under certain conditions, however, the treatment of the total distillate of the mineral oil with liquefied sulphur dioxide presents an advantage. Such a mode of working forms the subject-matter of this invention. It is of advantage when it is required to make a lubricating oil which has been treated by the Edeleanu process. The lubricating oil fraction of petroleum oil, especially the portions of higher boiling point or higher specific gravity, can be mixed and treated more easily and thoroughly with liquid sulphur dioxide if it is still intermixed with the more easily volatile portions than when only the more viscous constituents are alone subjected to the treatment. The mixing of the total fraction with sulphur dioxide and the separation into two layers occurs far more easily and thoroughly than when the more viscous oil separated therefrom is subjected to treatment with liquid sulphur dioxide. By the use of a continuous or counter-current process, by the development of the continuous evaporation and by the use of several evaporators, the operation of the Edeleanu process has been so essentially simplified and cheapened that the application of this process to the total distillate of petroleum appears well worth while. The subsequent separation of the extract, as well as of the raffinate, into the several fractions presents no difficulties but on the other hand in many cases proceeds more smoothly than when the total distillate is subjected to fractionation before the treatment.

One can also find for the extract, in the case of gas oil for example, a special use for certain solvents, so that in this case also under these conditions there is a special use in the treatment with sulphur dioxide.

It is always of advantage, however, in using the total distillate to separate from this previously the most easily volatile benzine fraction, because, otherwise, during the evaporation of the sulphur dioxide from the extract and raffinate it is liable to happen that the most easily volatile hydrocarbons becomes mixed with the evaporated sulphur dioxide and subsequent separation of these is difficult. If, however, one starts from a total distillate topped to 100° C. the further working in the Edeleanu apparatus presents no difficulties. It has been found practicable in certain cases to separate the whole of the benzine, or even portions of the light oil fraction, particularly if the distillate contains much of the heavier constituents which are to be worked up to highly viscous lubricating oils. Such heavy lubricating oil fractions have hitherto been worked up only with the use of much sulphur dioxide, with or without a diluent, whereas now the working up presents no difficulties and, indeed, can be conducted in mixers without special mixing devices.

One of the advantages of the present method is that it makes possible the liquid-$SO_2$ treatment of wax containing distillates without interference from wax emulsions which would otherwise be formed at the low temperatures employed. The intermediate

fractions, such as gas oil, transformer oil and turbine oil, hold the wax in solution.

There is no variation in the conduct of the process. The proportion of sulphur dioxide used for working up the total distillate is always dependent upon the content of the total distillate in aromatic constituents and unsaturated compounds or other impurities, according to the degree of purity desired, and also to some extent on the content of heavy distillate. The larger the content of unsaturated aromatic compounds and the larger the content of heavy distillate, the more sulphur dioxide must be used. Speaking generally, however, it can be taken that the proportion of sulphur dioxide varies between 75 per cent and 200 per cent.

*Examples*

1. 1000 kg. of a Rumanian mineral oil, which has been freed of constituents which boil at 140° C. are treated with 150 vol. % of liquid sulphurdioxide at about −5° C. After a certain time separation into two layers takes place, which are parted from each other. The lower layer (extract) contains the unsaturated and aromatic hydrocarbons dissolved in the sulphurdioxide, while the upper layer (the refined product) consists essentially only of saturated hydrocarbons mixed with some liquid sulphurdioxide. The sulphurdioxide is evaporated in the well known manner from the separated solutions. The extract thus produced represents a mixture of various unsaturated and aromatic hydrocarbons, which are separated by fractional distillation, and first is obtained a fraction of 140° to 200° C., which essentially consists of aromatic hydrocarbons, and which may be used as an addition to gasoline in order to make it more knockproof. The second fraction from 220° to about 350° C. represents an oil suitable for Diesel motors, while the remainder may be used as a lubricant with a very low sticking point. From the refined product is obtained a first fraction up to about 220° C. by fractionation, which fraction can be used as gasoline. The next fraction, from 220° to 330° C. represents an excellent well burning illuminating oil. The following fractions serve as a base for the manufacture of excellent transformer-, turbine-, and motor oils, having the advantage that they are free from those substances which easily polymerize and are the cause of resin formation.

2. In the mixer of a set of apparatus which serves for carrying on the Edeleanu process in continuous operation as is commonly practiced, a continuous stream of Californian mineral oil is admitted from below, the boiling point of which oil starts at about 150° C. This is met by a stream of liquified sulphurdioxide coming from above. Through the mixture brought about when the two streams meet, the sulphurdioxide dissolves from the mineral oil the aromatic (unsaturdated) and the sulphur containing products. The extract flows off at the bottom, while from the upper part of the mixer the refined product mixed with a little of sulphurdioxide flows off.

After freeing the refined product from the sulphurdioxide, decomposition into several fractions by means of distillation is made. The several fractions excel by an extraordinarily low content of sulphur containing products. These are removed more thoroughly by manufacturing the total mineral oil, even from the fractions boiling at a higher temperature, than by treating the separated fractions with sulphurdioxide, since apparently the extraction of sulphur containing constituents is accomplished more easily if the extracting is done in the presence also of readily flowing hydrocarbons. Decomposition into the several fractions is accomplished in a similar way as was explained with Example 1.

The raffinate and extract are separated into the several fractions in the usual stills and at pressures commonly used in the petroleum industry.

In the foregoing description and in the claims it will be understood that by a "total distillate" is meant a comprehensive distillate secured prior to the fractionation of the crude oil into various cuts and containing all of the fractions from the light ends up to and including heavy lubricating oils. The total distillate will not include the residues and still bottoms, and may be topped.

What I claim and desire to secure by Letters Patent of the United States is:

1. The process for refining mineral oils comprising treating with liquid sulphur dioxide a total distillate having an end point of about 400° C., separating the treatment mixture into a raffinate portion and an extract portion, and removing the sulphur dioxide therefrom.

2. The process for refining mineral oils comprising treating with liquid sulphur dioxide a crude oil from which only the light ends and still bottoms have been removed, separating the treatment mixture into a raffinate portion and an extract portion, and removing the sulphur dioxide therefrom.

3. The process for refining mineral oils comprising treating with liquid sulphur dioxide a total distillate consisting of all the fractions from light ends to and including heavy lubricating oils, separating the treatment mixture into a raffinate portion and an extract portion, and removing the sulphur dioxide therefrom.

4. The process for refining mineral oils comprising treating with liquid sulphur dioxide a total distillate topped at about 100° C. and having an end point of about 400° C.,

separating the treatment mixture into a raffinate portion and an extract portion, and removing the sulphur dioxide therefrom.

5. The process according to claim 1 in which the raffinate and extract are separately distilled to secure the desired fractions.

6. The process according to claim 2 in which the raffinate and extract are separately distilled to secure the desired fractions.

7. The process according to claim 3 in which the raffinate and extract are separately distilled to secure the desired fractions.

8. The process according to claim 4 in which the raffinate and extract are separately distilled to secure the desired fractions.

IGNAZ ROSENBERG.

## CERTIFICATE OF CORRECTION.

Patent No. 1,908,646. May 9, 1933.

IGNAZ ROSENBERG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 38, for "200°C." read "220°C."; 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 6th day of June, A, D. 1933.

M. J. Moore.

(Seal) Acting Commissioner of Patents.

separating the treatment mixture into a raffinate portion and an extract portion, and removing the sulphur dioxide therefrom.

5. The process according to claim 1 in which the raffinate and extract are separately distilled to secure the desired fractions.

6. The process according to claim 2 in which the raffinate and extract are separately distilled to secure the desired fractions.

7. The process according to claim 3 in which the raffinate and extract are separately distilled to secure the desired fractions.

8. The process according to claim 4 in which the raffinate and extract are separately distilled to secure the desired fractions.

IGNAZ ROSENBERG.

## CERTIFICATE OF CORRECTION.

Patent No. 1,908,646. May 9, 1933.

IGNAZ ROSENBERG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 38, for "200°C." read "220°C."; 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 6th day of June, A, D. 1933.

M. J. Moore.

(Seal) Acting Commissioner of Patents.