

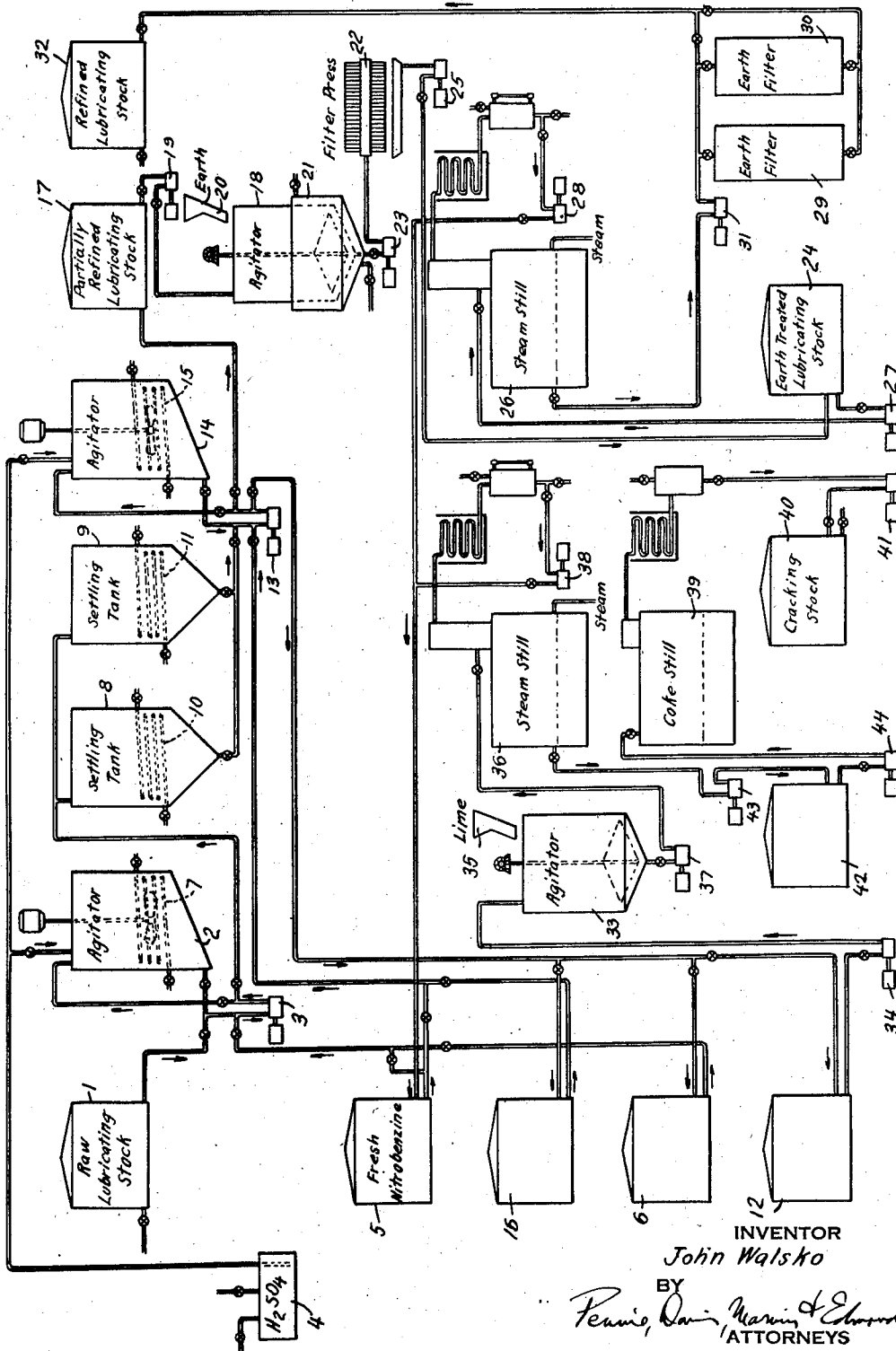
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ART OF REFINING HYDROCARBON OILS

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ART OF REFINING HYDROCARBON OILS

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8 Claims. (Cl. 196—13)

This invention relates to improvements in the refining of lubricating oils derived from petroleum. In referring to lubricating oils I refer to oils having a viscosity upward of 70 seconds at 100° F. Saybolt-Universal.

I have discovered that a number of important advantages, with respect to the product produced and with respect to the refining process, are secured by subjecting such lubricating oil stocks to treatment with nitrobenzene and sulphuric acid at the same time. The treatment of the oil with nitrobenzene and sulphuric acid at the same time secures advantages which are not secured by the use of nitrobenzene alone or by the use of sulphuric acid followed by the use of nitrobenzene or by the use of nitrobenzene followed by the use of sulphuric acid.

The advantages of the invention include particularly improvement of the stability of the refined product and improvement of the color of the refined product, and also include improvement of the viscosity index of the refined product, reduction of the Conradson carbon content of the refined product, and improvement of the demulsibility of the refined product, and, with respect to the refining process, the advantages include particularly improved recovery of the refined oil and also include more rapid and more complete separation of the refined oil from the sludge and associated material.

In carrying out the invention, the raw lubricating oil stock is mixed simultaneously with nitrobenzene and with sulphuric acid, and the sludge and associated material are thereafter separated from the oil, the latter containing some dissolved nitrobenzene. The treatment of the raw oil with nitrobenzene and sulphuric acid is advantageously carried out as a succession of repeated treatments. The treatment, or each of the treatments, may be carried out at temperatures upwards of about 45° F., as high as 100° F. or higher, for periods of time longer at lower temperatures and shorter at higher temperatures, say 3 minutes at 100° F. and 60 minutes at 45° F., for example. The oil subjected to treatment may be de-waxed or partially de-waxed prior to treatment. If the oil subjected to treatment contains a substantial proportion of wax, separation of the sludge and associated material from the oil following the treatment or treatments is usually promoted by effecting the separation at higher rather than lower temperatures. Following separation of the sludge and associated material from the oil, after the treatment or the last of a succession of treatments, the oil is neutralized and

dissolved nitrobenzene is separated therefrom. A neutralization may be effected, for example, with an absorbent earth, with caustic soda, with ammonia or with lime. Neutralization of the oil by treatment with an absorbent earth is advantageous in the production of a refined oil of good color and bloom. Following separation of dissolved nitrobenzene, the oil may or may not be filtered through or treated with an absorbent earth, for example.

I have observed that, in the improved refining operation of the invention, qualities are developed in the refined product with total amounts of sulphuric acid substantially smaller than required to develop comparable qualities with sulphuric acid alone, so far as these qualities can be developed with sulphuric acid alone, and that at the same time improved recoveries of the refined product are secured. The simultaneous presence of the nitrobenzene apparently modifies the action of the sulphuric acid to make smaller amounts as effective, as refining agents, as larger amounts in the absence of the nitrobenzene, as well as to afford the advantages previously noted.

The invention will be further illustrated by the following examples of various applications of the invention. It is intended and will be understood that these detailed descriptions of specific applications of the invention are by way of exemplification and that the invention is not limited thereto.

Recovery of used motor oil

The original motor oil had a viscosity of 715 seconds at 100° F. and 68 seconds at 210° F., and a Conradson carbon content not exceeding 0.65. Following use this motor oil had a viscosity of 546 seconds at 100° F. and 62 seconds at 210° F., and a Conradson carbon content of 0.66. One portion of this used oil was treated with 50% by volume of nitrobenzene and 1.8 pounds per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. and separation of the sludge and associated material from the treated oil was effected at 50° F. The recovered oil had a viscosity of 645 seconds at 100° F. and 68 seconds at 210° F., and a Conradson carbon content of 0.48. Another portion of the used oil was treated with 50% by volume (on the oil treated in each instance) of nitrobenzene and 2.0 pounds per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. followed by separation at 50° F. in each of two successive treatments. The recovered oil had a viscosity of 580 seconds at 100° F. and 67 seconds at 210° F., and a Conradson carbon content of 0.31. Still

another portion of the used oil was treated with 50% by volume of nitrobenzene and 1.83 pounds per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. followed by separation at 50° F. in each of three successive treatments. The recovered oil had a viscosity of 567 seconds at 100° F. and 67 seconds at 210° F., and a Conradson carbon content of 0.20.

10 *Lubricating oil distillate from Gulf-Coast crude petroleum*

The raw lubricating oil stock had a viscosity of 748 seconds at 100° F. and 61 seconds at 210° F., and a gravity of 19.3 A. P. I. This raw stock was treated in one instance with 50% by volume of nitrobenzene and 2.5 pounds per barrel of 66° Bé. sulphuric acid for 15-60 minutes at a temperature of 45° F. followed by separation at 45° F. in each of two successive treatments, and in another instance with 50% by volume of nitrobenzene and 1.25 pounds per barrel of 66° Bé. sulphuric acid for 15-60 minutes at 45° F. followed by separation at 45° F. in each of four successive treatments. The refined products had viscosities of 458-489 seconds at 100° F. and 55-58 seconds at 210° F., and gravities of 23.0-25.3 A. P. I.

30 *Lubricating oil distillate from Gulf-Coast crude petroleum*

The raw lubricating oil stock had a viscosity of 318 seconds at 100° F. and 47 seconds at 210° F., and a gravity of 20.7 A. P. I. This raw stock was treated with 50% by volume of nitrobenzene and 0.25 pound per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. followed by separation at 45° F. in each of four successive treatments. The refined product had a viscosity of 224 seconds at 100° F. and 46 seconds at 210° F., and a gravity of 26.8 A. P. I.

40 *Lubricating oil stock from Gulf-Coast crude petroleum*

The raw lubricating oil stock had a viscosity of 5850 seconds at 100° F. and 147 seconds at 210° F. One portion of this raw stock was treated with 100% by volume of nitrobenzene and 2.5 pounds per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. followed by separation at 45° F. in each of two successive treatments. The refined product had a viscosity of 1674 seconds at 100° F. and 98 seconds at 210° F. Another portion of this raw stock was treated with 50% by volume of nitrobenzene and 1.25 pounds per barrel of 66° Bé. sulphuric acid for 60 minutes at 45° F. followed by separation at the same temperature in each of four successive treatments. The refined product had a viscosity of 1700 seconds at 100° F. and 97 seconds at 210° F. Still another portion of this raw stock was blown with air containing ozone for 8 hours while maintained at a temperature of 200° F. and then treated with 50% by volume of nitrobenzene and 1.25 pounds per barrel of 66° Bé. sulphuric acid for 3 minutes at 100° F. followed by separation at 45° F. in each of four successive treatments. The refined product had a viscosity of 1680 seconds at 100° F. and 101 seconds at 210° F.

70 *Refined lubricating oil from Pennsylvania crude petroleum*

The lubricating oil had a viscosity of 910 seconds at 100° F. and 85 seconds at 210° F. a gravity of 27.1 A. P. I. and a Conradson carbon content of 1.012. This lubricating oil was treated with

50% by volume of nitrobenzene and 1.25 pounds per barrel of 66° Bé. sulphuric acid for 60 seconds at 45° F. followed by separation at the same temperature in each of four successive treatments. The refined product had a viscosity of 716 seconds at 100° F. and 80 seconds at 210° F. a gravity of 29.8 A. P. I. and a Conradson carbon content of 0.364.

Following the simultaneous treatment with nitrobenzene and sulphuric acid, the sludge and associated material may be separated from the oil, for example, by settling or by centrifuging. The separation of the sludge and associated material from the oil may be promoted by including in the sulphuric acid as supplied to the treatment a minor proportion of sodium sulphate, say 5% by weight on the acid for example. The addition of water will sometimes promote the separation of the sludge and associated material from the treated oil, and is useful where the separation is to be effected at higher rather than lower temperatures. I have observed that, although the use of an appropriate proportion of sulphuric acid in conjunction with the nitrobenzene promotes rapid separation of the sludge and associated material, an excess of sulphuric acid will sometimes retard this separation. When the treatment with nitrobenzene and sulphuric acid is carried out as a succession of repeated treatments, the separation of the sludge and associated material following the first treatment usually proceeds more slowly than following successive treatments.

The nitrobenzene used in the treatment may be recovered for re-use almost completely from the sludge and associated material and from the treated oil. For example, it may be distilled from the sludge and associated material and from the treated oil following neutralization. Appropriate measures should be taken to avoid decomposition of the nitrobenzene by the formation of aniline; such decomposition can usually be avoided by steam distillation. The nitrobenzene may also be recovered for re-use from the treated oil containing dissolved nitrobenzene, for example, by chilling the oil to a temperature approximating 35-40° F. while superposed upon and in direct contact with a body of water. This latter procedure is not my invention but is the invention of Arnold C. Vobach. When the treatment with nitrobenzene and sulphuric acid is carried out as a succession of repeated treatments, the sludge and associated material separated from the oil in later treatments of the series may be utilized, in some cases with appropriate additions of fresh nitrobenzene and/or fresh sulphuric acid, as the treating mixture in earlier treatments of the series. Usually the capacity of the treating mixture is consumed much more completely in the earlier treatments of such a series than in the later treatments.

After separation of the nitrobenzene present from the sludge and associated material, the remaining sludge and associated material is with advantage reduced to coke to produce an oil distillate peculiarly useful as charging stock for cracking operations intended to produce motor fuel gasoline of high anti-knock value.

I have illustrated in the accompanying drawing, diagrammatically and conventionally, one arrangement of apparatus adapted for carrying out one embodiment of my invention.

Referring to the accompanying drawing, raw lubricating oil stock, which may have been dewaxed or partially de-waxed, is supplied to the

stock tank 1. Successive charges of this stock are supplied to the agitator 2 by means of pump 3. With each charge an appropriate amount of sulphuric acid is supplied from the blow-case 4 and an appropriate amount of nitrobenzene or of a sludge mixture including nitrobenzene is supplied from the tank 5 or the tank 6, respectively, by means of pump 3. A mixture of fresh nitrobenzene and such sludge mixture may be supplied to the agitator 2 instead of either alone by means of pump 3. The mixture is agitated in the agitator 2 for the desired period while the desired temperature is maintained, by circulation of a heating medium or a cooling medium through the coil 7, and the mixture is then pumped into one or the other of the settling tanks 8 and 9 by means of pump 3. In the settling tank a separation is effected while the desired temperature is maintained, by circulation of a heating medium or a cooling medium through the coil 10 or 11. From the settling tank, 8 or 9, the sludge and associated material is discharged to tank 12 by means of pump 13. The separated oil, containing some dissolved nitrobenzene, is supplied to the agitator 14 by means of pump 13. Assuming a treatment comprising four successive treatments with nitrobenzene and sulphuric acid, this oil is subjected to three successive treatments with nitrobenzene and sulphuric acid, or sludge mixtures including nitrobenzene and sulphuric acid, followed by separation of sludge and associated material in the agitator 14 while the desired temperature is maintained by circulating a heating medium or a cooling medium through the coil 15. Following each successive treatment, a separation is effected in the agitator and the sludge and associated material is discharged to one of the tanks 16, 6 or 12 by means of pump 13. On the same assumption, the first separated sludge and associated material may be discharged to tank 12, the second to tank 6 and the third to tank 16. The treating mixture in the first treatment carried out in the agitator 14 may consist entirely or largely of a sludge mixture from tank 16. Following the last separation of sludge and associated material in the agitator 14, the treated oil is discharged to the stock tank 17 by means of pump 13. This partially refined lubricating oil stock may be subjected to any desired further treatment, including of course separation of dissolved nitrobenzene.

The arrangement of apparatus illustrated provides for treatment of this partially refined lubricating oil stock with an absorbent earth both before and after a steam distillation for the recovery of nitrobenzene. Again referring to the accompanying drawing, successive charges of partially refined lubricating oil stock from the stock tank 17 are supplied to the agitator 18 by means of pump 19. With each charge an appropriate amount of an absorbent earth is supplied from the hopper 20. The mixture is agitated in the agitator 18 for the desired period while the desired temperature is maintained, by circulation of a heating medium through jacket 21, and the mixture is then pumped through the filter press 22 by means of pump 23. The oil separated from the earth in the filter press 22 is discharged to the stock tank 24 by means of pump 25. This stock is supplied to the steam still 26 by means of pump 27 in which still dissolved nitrobenzene is separated from the oil by distillation. The thus recovered nitrobenzene is returned to the tank 5 by means of pump 28. The oil remaining undistilled following separation of the nitrobenzene may be pumped through one or the other of the

percolation filters 29 and 30 by means of pump 31 to the stock tank 32. The filters 29 and 30 are charged, for example, with an absorbent earth.

The treatment of the partially refined lubricating oil stock in the agitator 18 may consist, for example, of agitation for 5 minutes at a temperature of 150° F. with 5% by weight of Olmstead earth. A similar treatment, followed by separation of the earth, may be applied to the oil following separation of nitrobenzene in the still 26 instead of percolation filtration. Either or both of these treatments with earth may also be carried out at higher temperatures. Following separation of the nitrobenzene, for example, the oil may be mixed with 5% of Olmstead earth and the mixture maintained at a temperature of 400–500° F. for 30 minutes. Such high temperature earth treatment of the partially refined lubricating oil stock, however, is not my invention but is the invention of Arnold C. Vobach.

The arrangement of apparatus illustrated provides for recovery of nitrobenzene from the sludge and associated material separated following the treatment or treatments of the oil stock with nitrobenzene and sulphuric acid by neutralization with lime followed by a steam distillation, and for recovery of the oil content of the remaining sludge mixture by reduction to coke. Successive charges of sludge mixture from the tank 12 are supplied to the agitator 33 by means of pump 34. With each charge an amount of lime required to neutralize the charge is supplied from the hopper 35. The neutralized mixture is pumped to the steam still 36 by means of pump 37. Nitrobenzene separated from the sludge mixture by distillation in the still 36 is returned to tank 5 by means of pump 38. The residual mixture from the steam still 36 is reduced to coke in the coke still 39, tank 42 and pumps 43 and 44 being provided for handling this residual mixture. The coke still distillate is discharged to the stock tank 40 by means of pump 41. This coke still distillate is peculiarly useful as charging stock for cracking operations intended to produce motor fuel gasoline of high anti-knock value.

The range of proportions, with respect to each other and with respect to the lubricating oil stock being treated, of the nitrobenzene and sulphuric acid simultaneously used in the combined treatment and the concentration of the sulphuric acid, may vary within wide limits. In general, acid concentrations in the range 93–98% H_2SO_4 are advantageous although more or less concentrated acid may be used. The total volume of nitrobenzene used may vary from less than 50% to more than 400% by volume on the oil. The efficiency of the operation is usually improved if the combined nitrobenzene and the sulphuric acid treatment is carried out as a succession of repeated treatments, particularly when sludge and associated material separated from the oil in later treatments of the series is utilized as the treating mixture in earlier treatments of the series. It will be apparent that the proportions of nitrobenzene and sulphuric acid and the concentration of the acid may be varied from step to step in such successive treatments. The proportion of sulphuric acid used in each treatment may vary, for example, from about 0.1 pound per barrel to as much as 10 pounds or more per barrel of oil treated.

In some instances, particularly when improvement of the viscosity index of the refined product is important, I have found that oxidation of the lubricating oil stock prior to the combined treat-

ment with nitrobenzene and sulphuric acid as illustrated in one of the foregoing examples, is particularly advantageous.

I claim:

- 5 1. In refining lubricating oil, the improvement which comprises subjecting the oil to the action of nitrobenzene and sulphuric acid at the same time the amount of nitrobenzene relative to the oil approximating 50%-400% by volume.
- 10 2. In refining petroleum lubricating oils having viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises dewaxing the oil and thereafter subjecting the oil to the action of nitrobenzene and sulphuric acid at the same time the amount of nitrobenzene relative to the oil approximating 50%-400% by volume.
- 15 3. In refining petroleum lubricating oils having viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises subjecting the oil to the action of nitrobenzene and sulphuric acid at the same time the amount of nitrobenzene relative to the oil approximating 50%-400% by volume and thereafter subjecting the oil to the action of an absorbent earth.
- 20 4. In refining petroleum lubricating oils having viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises subjecting the oil to action of nitrobenzene and sulphuric acid at the same time in successive treatments the total amount of nitrobenzene relative to the oil approximating 50%-400% by volume.
- 25 5. In refining petroleum lubricating oils hav-

ing viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises subjecting the oil to the action of nitrobenzene and sulphuric acid at the same time in successive treatments the amount of nitrobenzene relative to the oil approximating 50%-400% by volume and using as the treating mixture in an earlier treatment of the series sludge and associated material separated from the oil in a later treatment of the series.

6. In refining petroleum lubricating oils having viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises subjecting the oil first to oxidation and then to the action of nitrobenzene and sulphuric acid at the same time the amount of nitrobenzene relative to the oil approximating 50%-400% by volume.

7. In refining petroleum lubricating oils having viscosities upwards of 70 seconds at 100° F. Saybolt-Universal, the improvement which comprises subjecting the oil to the action of nitrobenzene and sulphuric acid at the same time the amount of nitrobenzene relative to the oil approximating 50%-400% by volume.

8. The process of treating petroleum stock containing asphaltic impurities which comprises agitating the stock with nitrobenzene in the presence of not over, approximately, 1% of sulphuric acid below the temperature at which the stock becomes completely miscible with the nitrobenzene, separating the nitrobenzene layer from the raffinate layer and removing the nitrobenzene from the raffinate layer.

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