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TECHNICAL OIL MISSION  
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PATENT APPLICATION

PROCEDURE FOR PARAFFIN OIL PROCESSING

## PROCEDURE FOR PARAFFIN OIL PROCESSING

The most favorable procedure for processing paraffin oil consists of diluting the oils with solvents or combinations of solvents. On cooling the paraffin is precipitated and the crude paraffin is separated. With the addition of a sufficient amount of an oil-separating substance a separation into layers is caused in the deparaffined oil solution separated from the crude paraffin. The layer thus obtained with the greater solvent content can then be passed back, completely or in part, to be used for subsequent crude oil treatment. If found necessary, the oil-separating substance is first removed. In this procedure the most varied substances or combinations of substances suitable for the removal of paraffin from oil can be employed as solvents or combinations of solvents. Combinations of benzene and sulfur dioxide or of benzene and acetone can be used, as can carbon halides, as exemplified by symmetric and asymmetric dichloroethane, trichloroethane, tribromoethane, symmetric tetrabromoethane, trichloroethylene, acetalenetetrachloride, monofluoroethane, difluorodichloroethane, pentafluoromonochloroethane, monofluoroethylene, hexafluoroethane, trifluoromonochloroethylene, chlorobenzene, fluorobenzene, m-fluorotoluene, m-difluorobenzene, 1,3,5, trifluorobenzene, or tetrahydrofuran or its mixtures with those solvents that cause good paraffin crystal formation, i.e. with ketones such as acetone or methylethylketone, or with aliphatic alcohols such as methanol, propanol, butyl alcohol, or amyl alcohol, or with nitriles such as acetonitrile, or with esters, i.e. ethyl, propyl, or isobutyl acetate or the corresponding carbon halides. To obtain a separation into layers, sulfur dioxide, ammonia or methanol can be employed.

In this procedure it was found to be especially advantageous if water-soluble organic solvents or mixtures containing them were employed as the solvents for the removal of the paraffin, and if the separation into layers was carried on in the presence of water with ammonia added. Combinations of benzene and acetone, or of tetrahydrofuran with water-soluble alcohols are suitable for the separation of the paraffin in this procedure.

Small amounts of ammonia are sufficient to effect the separation into layers, i.e. 3 to 5% introduced into the solvent. The requisite amount of water is also small. It amounts to 0.5 to 2% which is introduced into the solvent. The water may be passed into the solution of deparaffined oil independently of the ammonia or in its company.

The upper layer formed in the separation consists mainly of oil, relatively little solvent, and small quantities of ammonia and water. It can be freed from the solvent by distillation and also from the ammonia and water at no great cost. The lower layer consists of relatively little oil, large quantities of solvent,

and the remaining portion of the water. It can be freed from the ammonia and the water by distillation which is likewise inexpensive because of the small amount of the substances involved. The oils contained in both layers reveal appreciable chemical differences. The oil of the layer containing less solvent possesses a lower specific gravity, a higher viscosity index, and a lower coke test (Conradson) than the oil of the layer containing more solvent. On being separated into layers decomposition of the order of a selective extraction takes place.

A high-grade oil with a low solidifying point can be obtained by distillation from the layer containing less solvent (the upper layer). As has already been pointed out, this can be done without much cost. The layer containing more solvent (the bottom layer) can be processed further in various ways. For instance, it can also be freed from the solvent by distillation. Because of the large amount of solvent involved this distillation is expensive. However, it possesses the advantage of obtaining a paraffin-free extract which can be employed directly for admixing with asphalt. It differentiates itself thereby from the extracts obtained by the customary methods of extraction which always contain paraffin and are, therefore, unsuitable for admixing with asphalt. In many cases, especially when the oils to be treated are carefully freed of asphaltic and resinous matter before the removal of the paraffin, i.e. by careful distillation, by refining with the use of sulfuric acid, by selective solvents, or by treatment with liquid hydrocarbons that are gaseous at ordinary temperature like propane, it is advantageous to return, completely or in part, the layer containing the greater part of solvent, to the crude oil awaiting removal of paraffin. Here it serves to dilute the crude oil before the removal of the paraffin which can be done with freshly introduced solvent.

In this connection it is not necessary to remove the water from the solution that is to be returned. The water can be allowed to reach the crude oil awaiting removal of paraffin without fear, since it is held in solution by the water-soluble constituents of the solvent even when subjected to intense cooling. It, therefore, does not hamper the removal of the paraffin. A certain quantity of water is already present in the solution of deparaffined oil so that it is not absolutely necessary to return further quantities of water accompanied by or, alongside of, ammonia.

Several of the procedures of this process are explained in greater detail in the accompanying drawings. In these drawings corresponding parts have been indicated by similar reference symbols for the sake of clarity.

In the procedure illustrated by Fig. 1 the crude oil awaiting removal of paraffin flows through pipe (1) into a mixing device (2) in which it is admixed with a solution of deparaffined oil, large quantities of solvent which are conducted by pipe (3), and with fresh solvent flowing in through pipe (4). It then flows, if necessary over a heating device (5), into a condenser (6) where it may be cooled to -20 degrees. At this temperature it flows into a filter (7) where the crude paraffin is separated. The latter is conducted by pipe (8) into a distilling apparatus and there freed of the solvent. The vaporized solvent is condensed and returned by pipe (4). At (10) the crude paraffin is drawn off. The solution of deparaffined oil flows off from filter (7) into pipe (11) and from there into the mixing device (12) and is here mixed with small quantities of ammonia diluted with water which are introduced by pipes (13) and (14). The main body now flows, after further cooling in condenser (15), if it is found necessary, into a separator (16) and is here divided into two layers. The upper layer is conducted by pipe (17) into the distillation apparatus (18). From here the vapors are transferred to condenser (19), from which the ammonia flows into pipe (14) while the solvent is reconducted to pipe (4). The deparaffined oil flows off at (20) from the distillation apparatus. The bottom layer of liquid from separator (16), from which a part can be drawn off through pipe (21) and processed separately, flows through pipe (22) into the distillation device (23) in which the ammonia is vaporized. Through pipe (13) it is transferred back to the mixing device (12). The solution leaving the bottom of the distillation apparatus (23), which consists of relatively little oil but of large quantities of solvent, flows into pipe (3) and is returned to circulation without further distillation.

The washing of the crude paraffin which was separated by the filter can be done expediently by the counter-current treatment according to patent process (Patent Application I 77 679 IVd/23 b). The procedure illustrated by Fig. 2 can be advantageously followed. In this case the filtering device would consist of a number of filters ranged one behind the other (A -D). The crude oil is supplied by pipe (1), as illustrated by Fig. 1. It is then mixed in a mixing device with a solution of deparaffined oil containing a large amount of solvent which was carried in by pipe (3) and cooled in condenser (6) after being warmed in the heating device (5) if necessary. The main body now flows into filter (A) where it is decomposed. The filtrate flows, as illustrated in Fig. 1, directly into (24) and pipe (11) into a condenser (27). It is then carried into a mixing device (12) or, if filter (A) is coarse-meshed and made of wire gauze, it can be conducted to fine-mesh filter (A') through valve (25) and pipe (26). Here it is again filtered and then passed back to the mixing device by way of pipe (11) and condenser (27). It is here mixed with ammonia containing water from pipes (13 and 14), and then carried to the separator (16). The upper liquid layer formed here passes through pipe (17) into the distillation apparatus (18). The vapors are passed into a condenser (19) from which the ammonia is returned by pipe (14) into the collecting pipe (4).



The bottom layer from separator (16) can be further processed in various ways. It can flow through valve (28) and pipe (22) into the distillation apparatus (23) where the ammonia is removed which was returned through pipe (13) into the mixing device (12). The solution of deparaffined oil with the higher solvent content flows through pipe (29) into the mixing device (30) and is there admixed with the crude paraffin passing through pipe (31) by way of step (A) and, if necessary, by way of step (A'). It is then admixed with the filtrate coming from step (C) by way of pipe (32). The main body now passes from pipe (33) to filter (B). The filtrate formed here is conducted into pipe (3) and through this into mixing device (2). The paraffin flows from filter (B) through pipe (34) into mixing device (35) and is here admixed with filtrate from filter (D) and then passes through pipe (34) into filter (C). The filtrate formed here is returned through pipe (32) into the mixing device (30). From filter (C) the paraffin passes through pipe (37) into the mixing device (38) and is here admixed with fresh solvent from collecting pipe (4) and pipe (39). It then passes through pipe (40) into filter (D).

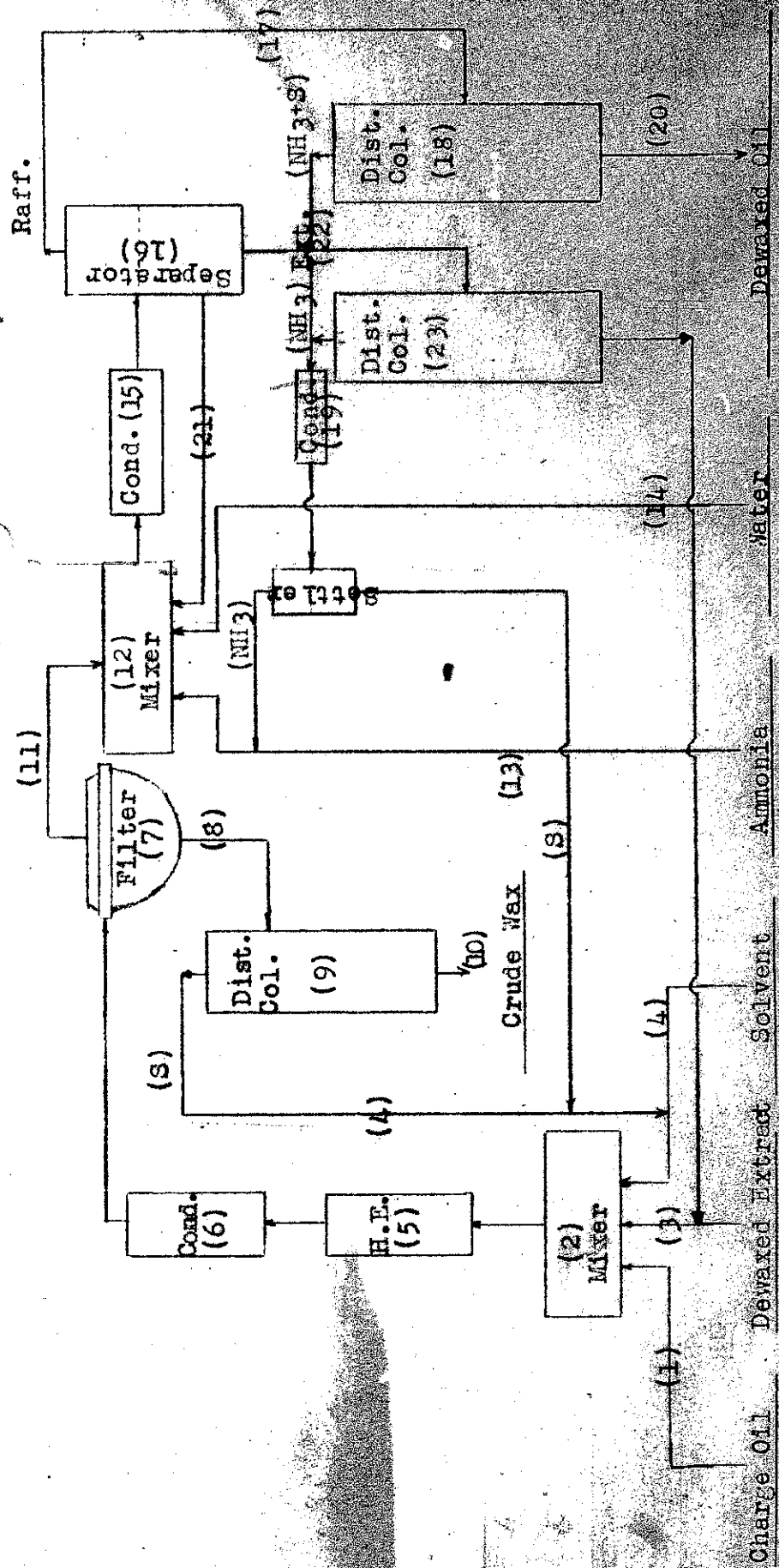
If so desired, the paraffin collected at filter (D) can again be decomposed, i.e. according to the procedure of patent (Patent application I. 77 680 IVd/23 b). For this purpose the liquid mass is conducted through pipe (42) and valve (44) to a heating device (45). It may there be warmed to 10 degrees and then admixed with solvent from collecting pipe (4) in mixing device (46). The mixture passes through pipe (47) to filter (E) and can be washed here with solvent also warmed to 10 degrees from pipe (49) which is equipped with a heating fixture. The hard oil-free paraffin that remains at the filter is conducted through pipe (50) into a distillation apparatus (51). Here the solvent is distilled off and its vapors pass into collecting pipe (52) and from there are conducted into pipe (4). The hard paraffin freed of solvent is drawn off at (53). The filtrate from filter (E) is cooled in cooling device (54) at about 0 degrees and, at this temperature, reaches filter (F). The paraffin that is separated at this point can be washed with solvent that comes from pipe (55) and can also be cooled to 0 degrees in condenser (56). The washed paraffin is conducted through pipe (57) to distilling apparatus (58). From here the solvent is likewise conducted to collecting pipe (52) while the paraffin is drawn off at (59). The filtrate from filter (F) is cooled in cooling device (60) at about -20 degrees and reaches filter (G). The paraffin separated here can also be washed with solvent from pipe (61) and also cooled at -20 degrees in condenser (62). The filtrate from filter (G) passes through pipes (63) and (39) back to the mixing device (38). The paraffin remaining at filter (G), which is composed of practically oil-free soft paraffin, is conducted through pipe (64) into the distillation apparatus (65), and is here freed of solvent which is also conducted into pipe (52). The soft paraffin is drawn off at (66).

The lower layer from separator (16) can also be processed in the same manner. It can be conducted into distillation apparatus (68) and here freed of solvent. The oil can be drawn off at pipe (69). The solvent vapors pass into condenser (70) from which the ammonia is conducted through pipe (71) into pipe (14) while the solvent passes through pipe (72) into collecting pipe (4).

#### EXAMPLE

10 kgs. of a lubricating oil containing 12.5% paraffin are dissolved in a mixture consisting of 31.44 kgs. of solvent, 1.56 kgs. of deparaffined oil and 2.27 kgs. of an extract of the above lubricating oil. Within an hour this mixture is cooled to -20 degrees. The solvent consists of 65 parts by weight of dichloroethane, 25 per cent by weight of tetrahydrofurane, 9 per cent by weight of methanol, and 1 per cent by weight of water. The crystallized paraffin is filtered by a large filter measuring 1.7 m<sup>2</sup> and washed together with a mixture of 10 kgs. of the above solvent and 1.17 kgs. of extract. The combined filtrates contain 11.88 kgs. of oil (including extract) and 35.2 kgs. of solvent. They are now mixed with 1.76 kgs. of ammonia at -20 degrees. Two layers are formed. The upper layer contains 8.44 kgs. of oil, 5.9 kgs. of solvent and .12 kgs. of ammonia. The ammonia is separated in a pressure column and the solvent separated in a column operating at ordinary pressure. 8.44 kgs. of oil with a solidification point of -19 degrees are obtained. The lower layer consists of 29.3 kgs. of solvent, 3.44 kgs. of extract, and 1.64 kgs. of ammonia. On removal of the ammonia it is returned and, as has already been described, used to dissolve fresh quantities of lubricating oil to wash the filtered paraffin. The crude paraffin which is removed at the filter contains 1.25 kgs. of paraffin, 1.87 kgs. of oil and 6.24 kgs. of solvent. It is slurried with 12.1 kgs. of fresh solvent, washed, and then again filtered. A crude paraffin is thereby obtained which contains 1.25 kgs. of paraffin, .31 kgs. of oil and 6.2 kgs. of solvent. The solvent is removed and an 80 per cent paraffin with a solidification point of 62.5 degrees remains. The washed filtrate contains 1.56 kgs. of oil and 12.14 kgs. of solvent. It is then returned and employed in dissolving fresh lubricating oil. Thus, within an hour 105 kgs. of lubricating oil distillate can be decomposed into 80 per cent paraffin and paraffin-free oil per m<sup>2</sup> of filter surface. Altogether only 5.9 kgs. of solvent and 1.76 kgs. of ammonia are needed to extract 8.44 kgs. of oil. Moreover, for the extraction of 1.25 kgs. of paraffin it is necessary to distill only 6.2 kgs. of solvent.

# FLOW SHEET DEWAXING PROCESS



to prove the correctness of the above given constitutional formula with hexyl-hexyl alcohol. We had no interest in the formation of fatty acids, and therefore a working hypothesis was assumed to the effect that the formation of fatty acids is not a result of the primary reaction, but rather of a secondary reaction which occurs with the formation of water; and that, should the formation of water take place under different circumstances, the reaction equilibrium could be shifted in favor of the alkyl alcohol.

The first series of experiments was therefore devoted to the study of the role played by the sodium concentration. Great experimental difficulties were encountered here, and the reaction products obtained could not be collected quantitatively to a satisfactory extent; the course of the reaction has therefore not yet been cleared up as far as its quantitative aspects are concerned.

Experiments for the confirmation of our hypothesis are still being continued.

Catalyst examinations in Me 245 (Dr. Geiseler).

Previous experiments have shown that iron precipitate catalysts with small additions of arsenic or antimony gave excellent results. Therefore, further experiments along this line were carried out with such catalysts; the catalysts contained about 0.1% As or Sb respectively; partly they were in pelleted form, and partly they were used in non-pelleted form.

1. Catalyst 4305 (96.2%  $\text{Fe}_2\text{O}_3$ , 3.5%  $\text{Al}_2\text{O}_3$ , 0.3% K)

Synth. temp. 200°, finished catalyst: 0.25% K (determined by spectro-analysis).



Fraction	Weight %	% Olefins	% Alcohol	Ester Number
33-200°	46.0	38.4	39.6	
200-230°	3.8	33.1	38.0	
230-350°	24.0	17.7	57.6	14.2
300-400°	7.0	10.9	47.2	
Above 400°	18.8	-	-	

2. Catalyst 4305/1 (96.2%  $\text{Fe}_2\text{O}_3$ , 3.5%  $\text{Al}_2\text{O}_3$ , 0.3% K, in 4 mm pellets)

Synth. temp. 206°

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
26-200°	59.8	45.3	40.3	
200-230°	3.3	28.4	31.9	
230-350°	19.0	19.5	40.8	0.0
350-400°	5.3	13.9	24.2	
Above 400°	10.0	-	-	

3. Catalyst 4303 (71.1%  $\text{Fe}_2\text{O}_3$ , 3.5%  $\text{Al}_2\text{O}_3$ , 0.3% K, 0.1%  $\text{As}_2\text{O}_5$ )

Synth. temp. 195°, finished catalyst: 0.24% K (det. by spectro-analysis)

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
27-200°	53.1	36.6	43.8	0.0
200-230°	3.9	19.1	42.8	0.0
230-350°	23.6	14.1	55.7	2.6
350-400°	6.2	11.7	30.0	-
Above 400°	11.4	-	-	-

4. Catalyst 4339 (96%  $\text{Fe}_2\text{O}_3$ , 3.5%  $\text{Al}_2\text{O}_3$ , 0.3% K, 0.1%  $\text{Sb}_2\text{O}_3$ )

Finished catalyst: 0.1% K (det. by spectro-analysis)

The experiment was discontinued owing to excessive synthesis temperature (203°C and still increasing).

5. Catalyst 4304 (96%  $\text{Fe}_2\text{O}_3$ , 3.5%  $\text{Al}_2\text{O}_3$ , 0.3% K, 0.1%  $\text{Sb}_2\text{O}_3$ ).

Synthesis temperature 202°, finished catalyst: 0.22% K (det. by spectro-analysis)

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
44-300°	57.3	29.5	46.3	
200-230°	2.5	18.0	42.2	
230-350°	21.2	14.0	50.4	12.7
350-400°	6.6	13.6	27.9	
Above 400°	10.9			

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