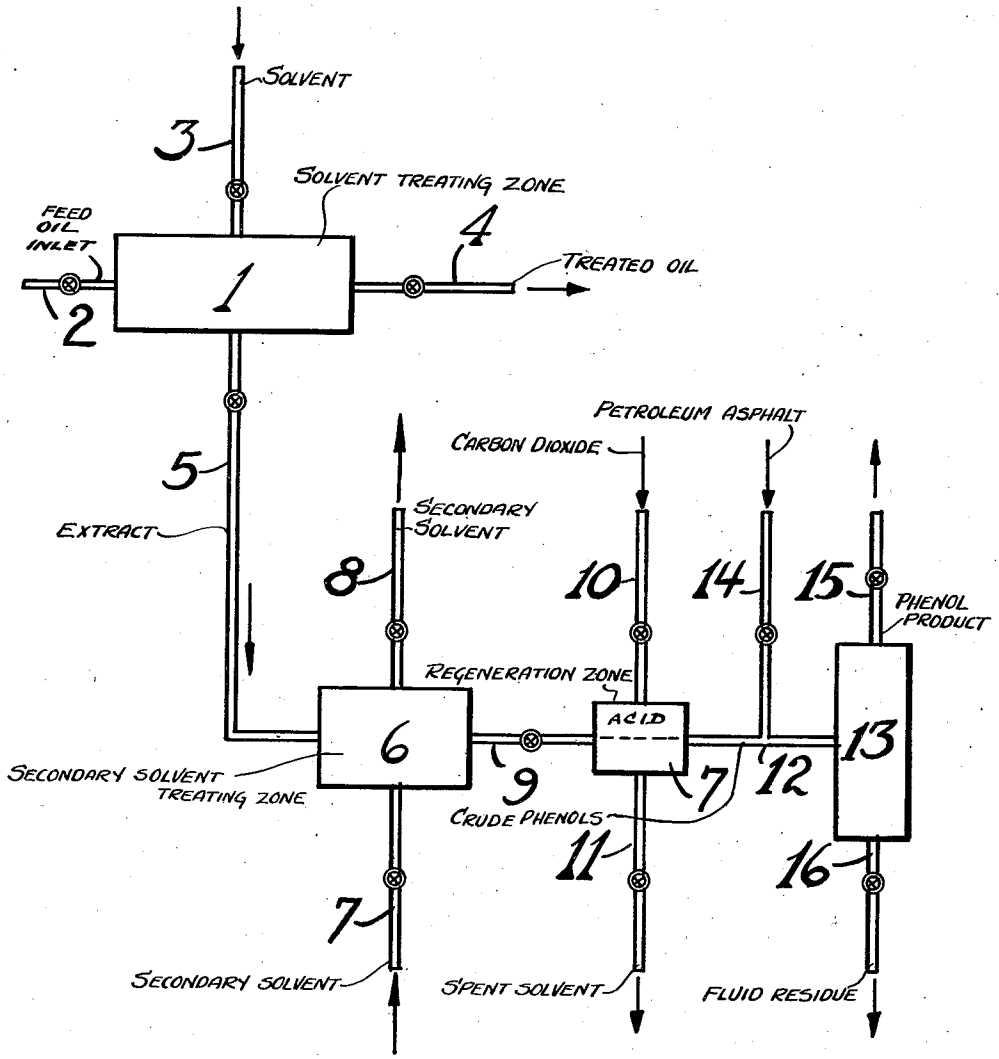
Nov. 10, 1942. R. A. GERLICHER 2,301,270

PROCESS FOR THE PRODUCTION OF PETROLEUM PHENOLS

Filed Nov. 9, 1940



Robert A. Gerlicher Inventor

By P. L. Young Attorney

Patented Nov. 10, 1942 2,301,270

UNITED STATES PATENT OFFICE

2,301,270

PROCESS FOR THE PRODUCTION OF PETROLEUM PHENOLS

Robert A. Gerlicher, Cranford, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application November 9, 1940, Serial No. 365,119

7 Claims. (Cl. 260—627)

The present invention is concerned with an improved process for the segregation and recovery of high quality naturally occurring acidic oxygen-containing compounds from oils containing the same. The invention is more particularly concerned with the recovery of naturally occurring high molecular weight petroleum phenols from petroleum oils containing the same. In accordance with the present process a petroleum oil fraction comprising naturally occurring high molecular weight phenols is segregated from a feed oil in an initial stage and then distilled in a secondary stage in the presence of a high molecular weight petroleum hydrocarbon such as a petroleum asphalt.

It is known in the art that valuable acidic oxygen-containing compounds such as naphthenic and phenolic type compounds are present in mineral oils, particularly in petroleum oils boiling in the lubricating oil, kerosene, heavy naphtha, and heating oil boiling ranges especially in those oil fractions derived from aromatic and naphthenic type crudes. These acidic oxygen-containing compounds are usually high molecular weight phenolic constituents having a rather complex structure which are usually recovered from cracked petroleum naphtha distillates, heating oil stocks, and other feed oils containing the same, by extraction operations utilizing various solvents. In general, the feed petroleum oil fraction containing these constituents, as for example a heating oil fraction, is treated with a strong aqueous or alcoholic caustic solution in order to form alkali metal phenolate salts. The alkali metal phenolate salts in the alkaline solution are separated from the oil and handled in a manner to recover and purify the segregated phenols. This is usually accomplished by treating the aqueous alkaline solution with a solvent such as a petroleum ether or naphtha to remove the residual hydrocarbon constituents.

The solution of the salts is then usually treated with carbon dioxide or with a weak mineral acid in a sufficient quantity to liberate the corresponding phenols which are removed as a crude phenol fraction. This crude phenol fraction contains various impurities and possesses a distinctive petroleum odor which in many cases prohibits their use. This is particularly true when it is desired to use the phenols for certain types of resins, since it is essential that the phenols which are to be utilized for this purpose contain less than 1% of oil and possess no objectionable petroleum odor. It therefore has been the practice to carefully distill the crude phenol product under vacuum conditions adapted to remove a distilled phenolic product overhead and to remove as a bottoms a hard pitch-like substance which comprised the undesirable impurities and decomposed phenols. This method of purification of the relatively high molecular weight phenols is undesirable in that the relatively high molecular weight phenolic type compounds are decomposed, resulting in an appreciable loss in yields of these desirable constituents. Furthermore, the decomposition of some of the phenols materially increases the difficulties of producing a relatively pure phenolic distillate product.

I have now discovered a process by which crude phenols secured in the manner described may be readily and efficiently handled to produce a pure, high-quality product without any appreciable loss in yields of the desired phenols occurring. In accordance with my invention the crude phenols are distilled in the presence of a relatively high-boiling, high molecular weight petroleum oil product, as for example a heavy asphalt. By operating in this manner a maximum overhead product is secured and a continuous distillation operation may be carried out since the bottoms remain in the fluid state and may readily be removed from the still. The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same.

For purposes of illustration it is assumed that the phenol containing feed oil is a segregated petroleum oil fraction boiling in the gas oil boiling range. The feed oil is introduced into solvent treating zone 1 by means of feed line 2. It is also assumed that the solvent comprises a strong aqueous or alcoholic caustic solution which is introduced into solvent treating zone 1 by means of line 3. Operating conditions are adapted to remove the naturally occurring high molecular weight phenols from the feed oil which is withdrawn from solvent treating zone 1 by means of line 4 and handled in any manner desirable. The aqueous solution of alkali metal phenolates is withdrawn from solvent treating zone 1 by means of line 5 and preferably introduced into a secondary solvent treating zone 6 in which it is contacted with a secondary solvent, as for example a petroleum ether or naphtha, which has the ability to dissolve the residual feed oil hydrocarbon constituents. For purposes of illustration it is assumed that the secondary solvent comprises a low boiling petroleum oil which is introduced into solvent treating zone 6 by means of line 7 and is withdrawn along with the residual hydrocarbon constituents by means of line 8. The alkali metal alcoholic solution of phenolates is then passed into regeneration zone 7 by means of line 9, in which the corresponding phenols are regenerated from the phenolate salts by means of carbon dioxide, which is introduced into zone 7 by means of line 10. The spent solution is withdrawn from zone 7 by means of line 11, while the crude phenol fraction is withdrawn by means

of line 12 and passed into distillation zone 13. Prior to introducing the crude fraction into distillation zone 13, it is mixed with a relatively high-boiling, high molecular weight petroleum fraction which for the purposes of illustration is assumed to be a petroleum asphalt. This fraction is introduced into the crude phenol fraction by means of line 14. Temperature and pressure conditions are adjusted in distillation zone 13 to remove overhead by means of line 15 high quality petroleum oil phenols, and to remove as a bottoms by means of line 16 a fluid residue.

The process of the present invention may be widely varied. The operation essentially comprises distilling crude petroleum phenols in the presence of an added high molecular weight, high-boiling petroleum residue under conditions in which the yield of overhead refined phenols is increased and in which excessive polymerization and decomposition of valuable crude phenols is prevented. The process may be adapted for the treatment of crude phenols secured from any mineral oil by any conventional procedure. However, the operation is particularly adapted for refining crude phenols secured from petroleum oils, particularly relatively high molecular weight crude phenols segregated from petroleum oils boiling in the gas oil, heating oil and higher boiling ranges.

A particularly desirable method for segregating these naturally occurring phenols from phenols from phenol containing petroleum oils is to treat the petroleum oil with a suitable alkali, as for example sodium or potassium hydroxide or the like, in order to form the alkali metal phenolates. The neutralizing temperature employed is preferably atmospheric, although other temperatures may be utilized. The amount and concentration of the alkali used in the neutralization stage will be sufficient to secure substantially complete conversion of the phenols to the corresponding alkali metal phenolates. In general it is preferred to use from 0.02 to 0.05 volume of alkali solution per volume of phenol containing feed oil. Under these conditions the concentration of the alkali should preferably be in the range from about 10% to 40%. It is, however, to be understood that the concentration and amount of alkali employed will depend upon the concentration of the phenols in the phenol containing oil. It is necessary in order to secure high yields of purified phenols that an excess amount of alkali be employed in order to prevent the hydrolysis of the alkali metal phenolates to the corresponding phenols.

The solvent used to remove the residual constituents of the feed oil from the alkali metal phenolates may be any suitable solvent which will dissolve these oil constituents. In general, solvents of the class of lower boiling petroleum hydrocarbons are employed, specific examples of which are solvent naphtha and petroleum oils boiling in the motor fuel boiling range. The quantity of solvent used in the primary alkali metal phenolate treating stage will depend upon the particular solvent being used and the amount and character of the residual petroleum oil constituents present. In general, it is preferred to use from about one-half to four volumes of solvent per volume of alkali metal phenolate solution. The temperature and pressure conditions employed in the solvent treating stage likewise depend upon the particular solvent used and the character of the residual oil being separated from the alkali metal phenolates. In general, it is preferred to use atmospheric pressure and a temperature in the range from about 80° F. to 120° F.

The alkali metal phenolate solution is acidified by treatment with any suitable acid, as for example sulfuric acid, hydrochloric acid, and the like. In general, it is preferred to regenerate the corresponding phenols from the phenolate salts by treatment with carbon dioxide and to separate the liberated phenols from the spent aqueous solution.

Although the above described method of segregrating the crude phenol fraction from the phenol containing petroleum oil is generally employed, it is to be understood that crude phenols segregated by any suitable means may be likewise treated in accordance with the present process. For example, the present operation is particularly adapted for the refinement of relatively high molecular weight phenols and naphthenic acids segregated from feed oils containing the same by use of various adsorbents such as various zeolites, bauxite, and the like.

The crude phenols, segregated in the manner described, are blended prior to distilling the same with a relatively high molecular weight petroleum hydrocarbon. In general, these materials should have a gravity in the range from about 10.0 to about 15.0° A. P. I. and boil in the range above about 220° C. at 10 mm. Hg (absolute). A particularly desirable addition agent comprises a heavy petroleum asphalt having a gravity of about 13.0 to about 14.0° A. P. I.

The amount of the addition agent added will depend upon the character of the crude phenols and the particular high molecular weight petroleum hydrocarbons added. In general the amount of heavy petroleum oil added is in the range from about 5% to about 30%, preferably from about 15% to 25%.

In order to further illustrate the present invention, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

EXAMPLE 1

Various crude petroleum phenol fractions were distilled in a number of operations. The results secured when employing a high molecular weight petroleum oil as compared to operations in which the petroleum oil was not employed are as follows:

Crude phenol fraction distilled

	Without added high boiling—		With addition of pet. asphalt having A. P. I. gravity of 13.4°
	Pet.	Oil	
Carrier	None	Steam	Steam
Final bottoms temp., °C	220	210	250
Absolute pressure, mm. Hg	10	10	10
Percent petroleum asphalt added			20
Yield percent overhead	70	81.4	86.8
Nature of bottoms	Hard Pitch	Hard Pitch	Fluid
Per cent unsaponifiable in overhead[1]	2.23		2.04

[1]The unsaponifiabe (oil content) was determined by saponifying the phenols using an excess of 20% sodium hydroxide solution; extracting the soap with petroleum ether and weighing the residue after evaporation of the ether.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the production of high quality phenols from crude phenol fractions segregated

from mineral oils comprising distilling a feed crude phenol fraction in the presence of an added high molecular weight petroleum asphalt under conditions to remove overhead the refined phenols and to remove as a fluid bottoms product the added hydrocarbon and the impurities present in the feed phenol fraction.

2. Process in accordance with claim 1 in which said crude phenol fraction is segregated from a petroleum oil and in which the added petroleum asphalt comprises a petroleum asphalt having a gravity in the range from about 10.0 to about 15.0° A. P. I.

3. Process in accordance with claim 1 in which said feed phenol fraction comprises high molecular weight naturally occurring phenols and in which about 5.0 to about 30.0% of a petroleum asphalt having a gravity in the range of about 10.0 to about 15.0° A. P. I. is added.

4. Process for the segregation and recovery of high quality phenols from petroleum oils containing the same comprising treating a petroleum feed oil with a caustic solution under conditions to convert the phenols to corresponding alkali metal phenolates, separating the alkali metal phenolates from the treated feed oil, reextracting the separated alkali metal phenolates with a solvent having the ability to dissolve residual feed oil constituents, separating the alkali metal phenolates, liberating the phenols and distilling the same in the presence of an added high molecular weight petroleum asphalt having an A. P. I. gravity in the range from about 10° to about 15°, under conditions to remove overhead the refined phenols and to remove as a fluid bottoms product the added hydrocarbon and the impurities present in the feed phenol fraction.

5. Process in accordance with claim 4 in which the added high molecular weight petroleum asphalt comprises a petroleum asphalt having a gravity in the range from about 13° to about 14° A. P. I.

6. Process for the segregation and recovery of high quality phenols from petroleum oils containing the same comprising treating a petroleum feed oil with a zeolite under conditions to remove the phenols from the feed oil, removing the treated oil and treating the zeolite to recover the phenols therefrom, then distilling the crude phenol fraction in the presence of an added high molecular weight petroleum asphalt having an A. P. I. gravity in the range from about 10° to 15°, under conditions to remove overhead the refined phenols and to remove as a fluid bottoms product the added hydrocarbon and the impurities present in the feed phenol fraction.

7. Process in accordance with claim 6 in which said feed phenol fraction comprises high molecular weight naturally occurring phenols and in which the added high molecular weight petroleum hydrocarbon comprises about 5.0 to about 30.0% of a petroleum asphalt having a gravity in the range of about 10.0 to about 15.0° A. P. I.

ROBERT A. GERLICHER.