

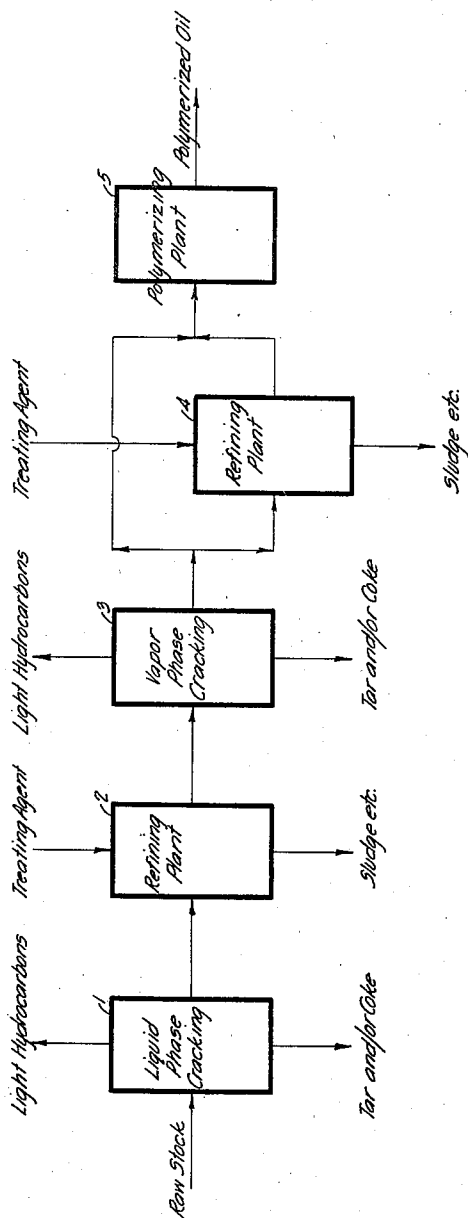
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METHOD OF TREATING OILS

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METHOD OF TREATING OILS

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This invention pertains to the manufacture of olefines from relatively high boiling initial hydrocarbon materials, and more specifically deals with a process in which the yield and quality of the olefines produced from such high boiling oils is so improved, as to increase the yield of lubricating oils, spindle oils, transformer oils, Diesel oils, etc., produced by polymerization of said olefines.

In the manufacturing of such mineral oils as, for example, synthetic lubricating oils, by polymerization of unsaturated hydrocarbons obtained by cracking, it has been customary to subject the initial material to a vapour phase cracking process before refining it, since it was thought that a higher yield of the most suitable olefines could be obtained in this way than by using a liquid phase cracking process.

This method, however, has serious disadvantages, especially in the case of oils containing only a small amount of volatile components. The conversion of such oils into the vapour phase presents many difficulties, even though the cracking be effected in the presence of steam, hydrogen, cracking gases, etc. With a high boiling material, very large quantities of such gases are required and the process becomes wasteful and uneconomical.

Moreover, various impurities present in the oil, such as nitrogen and sulphur compounds, not only tend to form deposits of carbon on the cracking apparatus, but also contaminate the final product and detract from its value.

Finally, when the refining process consists in a treatment with selective-solvents applied after a vapour phase cracking, there occurs a considerable loss of lower olefines, which are a product valuable for the manufacture of, for example, lubricating oils. This loss is due to the fact that the olefines are readily soluble in many of the solvents used, such as, for example, liquid sulphur dioxide.

I have now discovered that all these disadvantages may be easily remedied, and that higher yields of olefines capable of producing by polymerization lubricating oils of superior quality may be obtained by using the method of my invention.

Briefly, this method consists in cracking the initial stock in the liquid phase, subjecting the products of cracking to a refining treatment, and then re-cracking them in the vapour phase. If desired, a second refining treatment may then be applied.

According to my process, any mineral oil may

be used as initial material, but preferably such materials which consist of relatively non-volatile hydrocarbons or contain substantial amounts thereof, such as paraffin wax, wax tailings, paraffinous shale oil, paraffinous distillates, ozokerite, ceresine, residues of brown coal-tar treatment, etc., are used. The initial material is subjected to cracking in the liquid phase, according to any conventional method, and any conventional catalysts may be used if desired.

The cracking conditions should be preferably be adjusted so as to give a main fraction boiling approximately between 300° and 850° F. which according to the prior art is most readily achieved at temperatures between about 800° and 900° F. At these temperatures formation of a certain amount of aromatics invariably takes place, some of which aromatics boil within the boiling range of the main fraction. This fraction is subjected to a refining treatment with the object of removing aromatics, nitrogen and sulphur compounds which contaminate the oil. This treatment may be effected as an extraction process using such selective solvents as liquid sulphur dioxide, nitrobenzol, furfural, phenol, BB' dichloroethyl ether, alcohol ether, acetone-benzol, etc. The simultaneous use of more than one of these solvents, or their mixtures, in a counter-current process will also give excellent results.

Instead of an extraction process, the products of the liquid phase cracking may be subjected to refining with adsorption agents such as clay, bauxite, fuller's earth, diatomaceous earth, silica gel, etc. It is particularly advantageous to apply such treatment to the oil at a relatively high temperature, since in that case the acidic impurities contained in the oil, such as naphthenic acid, sulphonic acid, etc., are completely removed by the adsorptive treatment.

It is also possible to treat the selected fraction with sulphuric acid of a suitable concentration, whereby undesirable oxygen, nitrogen and sulphur compounds, as well as substances containing phenols and amines, are removed as sludge. The product may then be neutralized with lye or other suitable alkali.

After the selected fraction has been refined by any of the above means, it is again cracked, this time in the vapour phase under conditions known to be conducive to the formation of olefines from non-aromatic hydrocarbons boiling between 300° and 850° F., and preferably at a higher temperature of about 1000°-1100° F. Again, the cracking may be effected in the presence of desired catalyst. After condensation,

the liquid products obtained may be re-treated for the removal of undesirable compounds formed during the vapour phase cracking, such especially as the diolefines. This treatment may be

5 physical, such as distillation, or chemical, for example, a refining treatment at an elevated temperature with aluminium or zinc chloride, which gives especially good results.

To more fully explain my invention, reference is had to the drawing which represents a flow diagram of my process.

Raw stock of the type hereinbefore described enters liquid phase cracking plant 1 from a source not shown. In this plant the stock is cracked under conditions to produce a large middle fraction, some light hydrocarbons and tar and/or coke. The middle fraction which preferably boils between about 300° and 850° F. is taken to refining plant 2, while the other incidental products of the cracking are discarded from this process. During the treatment in refining plant 2, aromatics and/or non-hydrocarbon impurities are removed from the middle fraction, which now is transferred to vapor phase cracking plant 3. In the vapor phase cracking plant a distillate rich in olefines is produced, which, after suitable fractionation, is treated in refining plant 4 for the removal of diolefines, aromatics and other impurities which tend to interfere with the manufacture of stable lubricating oils by polymerization, and then is polymerized in polymerization plant 5; or else the distillate may go directly from the vapor phase cracking plant 3 to polymerizing plant 5 without passing through refining plant 4.

Example

275 gallons of paraffinous Pacura oil were cracked in the liquid phase at 850° F. under reflux of all constituents boiling above 750° F. The following yield was obtained:

	Gallons
Gasoline (F. B. P. 400° F.)	38
Oil (F. B. P. 750° F.)	223
Fuel oil	14

The 223 gals. of oil obtained were subsequently treated with liquid SO₂, yielding 190 gals. of raffinate. The raffinate was then cracked in the vapour phase at 1050° F. The following yield was obtained:

Gas	kgs.	130
Unsaturated oil	gals.	116
Fuel oil	gals.	38

The unsaturated oil was then polymerized with AlCl₃, giving a stock from which more than 83 gallons of excellent lubricating oil were manufactured. Moreover an oil which is very well suited for use in Diesel engines and a spindle oil were obtained during the process.

I claim as my invention:

1. In the process of producing olefines, which are capable of being converted to stable lubricating oils by polymerization with an active catalyst of the type of aluminum chloride, from a hydrocarbon oil containing not more than a relatively small amount of volatile components, an improvement which comprises the steps of cracking said oil in the liquid phase in the absence of excess hydrogen under a superatmospheric pressure at a cracking temperature for a time sufficient to convert a portion of said oil into aromatic hydrocarbons boiling within the range from 300° to

850° F., separating from the cracked oil a fraction boiling below about 850° F., containing said aromatic hydrocarbons, subjecting said fraction to a refining treatment capable of removing at least a substantial portion of said aromatic hydrocarbons, and cracking the refined fraction containing a substantially diminished amount of aromatic hydrocarbons in the vapor phase at a temperature higher than the liquid phase cracking temperature for a time sufficient to increase substantially the content of olefines without a substantial increase in the aromatic content of the fraction.

2. In the process of producing olefines which are capable of being converted to stable lubricating oils by polymerization with an active catalyst of the type of aluminum chloride from a hydrocarbon oil containing sulfur compounds, and not more than a relatively small amount of volatile components, an improvement which comprises the steps of cracking said oil in the liquid phase in the absence of excess hydrogen under a superatmospheric pressure at a cracking temperature for a time sufficient to convert a portion of said oil into aromatic hydrocarbons boiling within the range from 300° to 850° F., separating from the cracked oil a fraction boiling below 850° F., containing said aromatic hydrocarbons and sulfur compounds, subjecting said fraction to a refining treatment capable of removing at least a substantial portion of said aromatic hydrocarbons and sulfur compounds, and cracking the refined fraction containing a substantially diminished amount of aromatic hydrocarbons and sulfur compounds in the vapor phase at a temperature higher than the liquid phase cracking temperature for a time sufficient to increase substantially the content of olefines without a substantial increase in the aromatic content of the fraction.

3. The process of claim 1, wherein the liquid phase cracking is effected in the presence of a cracking catalyst.

4. The process of claim 1, wherein the fraction boiling below 850° F. is refined by extracting said products with a preferential solvent for aromatic hydrocarbons.

5. The process of claim 1, wherein the fraction boiling below 850° F. is extracted with a solvent chosen from the following group: liquid sulphur dioxide, nitrobenzol, furfural, phenol, BB' dichlorethyl ether alcohol-ether mixture, acetonebenzol mixture and wherein the raffinate is the refined fraction.

6. The process of claim 1, wherein the fraction boiling below 850° F. is refined by treatment with an adsorption agent.

7. The process of claim 1, wherein the fraction boiling below 850° F. is refined by treatment with sulphuric acid.

8. The process of claim 1, wherein the vapour phase cracking is effected in the presence of a cracking catalyst.

9. The process of claim 1, wherein the products of vapour phase cracking are subjected to chemical refining treatment to remove diolefines.

10. The process of claim 1, wherein the products of vapour phase cracking are subjected prior to polymerization to a refining treatment under polymerizing conditions using a catalyst chosen from the following group: aluminium-chloride and zinc-chloride.

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