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## METHOD OF REFINING CRACKED OILS

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1 Claim. (Cl. 196—44)

The present invention relates to a method of refining cracked oil, characterized in that by adding to cracked oil at the ordinary temperature or below it one or more of copper, lead, zinc and iron salts of abietic acid, oleic acid, and naphthenic acid in solid state or as dissolved in one or mixture of two or more of gasoline, petroleum, benzol, toluol, xylols, or turpentine, all the compounds of offensive odor and other impurities contained in cracked oil may not only be combined with metal or metals in dissolved state and be precipitated as insoluble salts together with the compounds of offensive odor, but also even disagreeable smell compounds very difficult to react may be adsorbed and precipitated at the same time.

The object thereof is to bring all of principal sources of offensive odor such as thioalcohols contained in cracked oil into intimate contact at a comparatively low temperature with metallic salts of organic acids soluble in cracked oil, to make them react upon each other directly by double decomposition and precipitate as insoluble salts, and at the same time to make compounds, which are very difficult to react with ordinary refining agents, such as disulphides deposited by the astringent and adsorptive actions of these insoluble salts at the moment of their formation, thus removing these sources of disagreeable odor completely from cracked oil without any operation detrimental to volatile oil, such as agitation, stirring, etc.

This invention relates to a method of refining the cracked oil produced by the cracking process of petroleum oils, the tars manufactured from coal and shale, and other organic matters and is adapted mainly for removing completely the bad smell compounds contained in cracked oil and at the same time for increasing the stability of the product.

The bad smell sources in cracked oil are chiefly thioalcohols, di-sulphides and unsaturated organic compounds, above all, low boiling thioalcohols. These substances even in the slightest quantity can give offensive smell to volatile oil. For instance, ethyl thioalcohol can still give disagreeable smell to gasoline even with the concentration $\frac{1}{10000}$ or $\frac{1}{100000}$ by weight.

Thioalcohol gives out offensive smell lesser with the increase of its molecular weight, but even crystallizable higher member of thioalcohol has bad smell, and thioalcohol is liable to reduce its reactive power gradually with the increase of its molecular weight.

In cracked oil, the quantity of disulphide originally present in it is only very small, the majority being produced by the oxidation from thioalcohol and consequently its quantity increases gradually with the lapse of time after the manufacture of cracked oil. This compound is also the cause for giving a kind of burning smell to cracked oil. It is extremely difficult to react with ordinary refining agents for cracked oil and consequently is difficult to remove.

Some unsaturated organic compounds in cracked oil are very unstable. If isolated, they will mostly polymerize at once, but if diluted with gasoline, they will become comparatively more stable. They give a kind of disagreeable odor to cracked oil by their oxidation products. However, they may be removed easily by treatment with sulphuric acid.

Now, according to the present method which is the result of the study of the constitutions and properties of many such bad smell compounds these bad smell sources may be removed completely.

The known methods all employ refining agents insoluble in the object to be purified, so that even by any violent agitation the intimate contact of a refining agent with the object to be purified is difficult, more so when their difference in the specific gravity is greater. Therefore, only a portion, but not the whole, of these bad smell compounds are removed and consequently the complete removing of the bad smell source cannot be expected. In the refining operation, the oxidation of thioalcohols is accelerated more and more with the violency of agitation in the atmosphere and therefore this agitation operation does not only make thioalcohols stay as disulphides, but also causes the loss of gasoline due to volatilization and consequently the decrease of the yield of the product.

The inventors have isolated various kinds of thioalcohols from cracked oil and manufactured various kinds of disulphides therefrom, and then studied their reactions with various kinds of metals and metallic salts of organic and inorganic acids and their various properties including solubilities, stabilities, etc. Also they have studied the easiness and speed of the formation of metallic salts from the solutions of thioalcohols and disulphides in petroleum hydrocarbon, and the behavior of these salts in petroleum hydrocarbons. Thus, by applying the results of these studies to cracked oil and studying the best condition with regard to the refining of cracked oil, they have succeeded in discovering the following matters:—

1. One or a mixture of copper, lead, zinc and iron salts of abietic acid, oleic acid and naphthenic acid are easily soluble in gasoline, petroleum oil, benzol toluol, xylols, turpentine, etc., and, when kept as concentrated solutions, they do not change their qualities.

2. If a solution of metallic salts of these organic acids is added to gasoline or petroleum oils containing thioalcohols, it disperses throughout the latter spontaneously, mixes with it and

reacts with thioalcohols by double decomposition even at the ordinary temperature or below it, depositing metallic salts of thioalcohols. Thus, by this way it is possible to remove thioalcohols completely from the oil.

As to the reaction taking place in this process, the inventors have studied it fully with regard to abietic acid and oleic acid. It is illustrated by the following equation of the reaction of propyl thioalcohol with abietate:—

(I) $2C_3H_7SH+Cu(C_{20}H_{29}O_2)_2=Cu(SC_3H_7)_2+2C_{20}H_{30}O_2$

$Cu(SC_3H_7)_2$ produced here is also converted into disulphide and cupric salt of propyl thioalcohol directly after it is produced.

(II) $4Cu(SC_3H_7)_2=2CuSC_3H_7+(C_3H_7S)_2$

3. Disulphide produced here is mostly adsorbed into metallic salt of thioalcohol the instant it is produced and is deposited with salt if the product is allowed to be settled spontaneously without stirring and presents the appearance as if this refining reaction had occurred according to only the Equation (I).

4. If a solution of iron salt of abietic acid is added slowly to gasoline containing thioalcohol together with the above copper salt solution in such proportion that the former is 20–50% of the latter and the mixture is left alone, the disulphide produced by the above reaction is deposited simultaneously with the salts of thioalcohol by astringent and adsorbing actions of the salts.

5. It is necessary that the reaction between metallic salt of organic acid and thioalcohol should proceed slowly. Thus, after the completion of the reaction and the deposition of metallic salt of thioalcohol and disulphide, the supernatant oil is filtered gently through fuller's earth filtering bed and thus these bad smell sources may be separated from the oil to be purified completely.

6. The refined cracked oil may be subjected to steam distillation directly. After the part of gasoline fraction is distilled, the residual oil is stirred with alkali solution and thus abietic acid may be recovered as alkali soap from the oil.

7. Copper salt of abietic acid may be recovered by adding the necessary quantity of fresh abietic acid to the alkaline solution of the recovered abietic acid soap, thus converting it into alkali soap and then adding the necessary quantity of a solution of copper sulfate.

8. The recovered copper abietate may be employed repeatedly with the same effect as the originally prepared salt for precipitation of thioalcohol.

When the result of the above study was applied to the refining of cracked oil, it was possible to produce cracked gasoline entirely free from thioalcohols and the bad smell of disulfides.

The following are a few examples of refining of cracked oil for the preparation of cracked gasoline:—

(1) Add 0.5% (by volume) of 20% caustic soda solution to 100 kilolitres of the cracked oil produced from Dubb's cracking plant and agitate it to remove sulphuretted hydrogen, organic acids and other reactive substances from the cracked oil. This pre-treatment economizes metallic salt of organic acid to be required. Next, after washing it with water enough to remove alkali-residue completely, dehydrate it. Then, add clear extract solution of copper resinate in gasoline, which is prepared by settling and filtering a solution of 200 kilograms of copper resinate in 500 litres of gasoline, to the above cracked oil purified by alkali solution and leave the mixture for 8 to 12 hours to settle down insoluble salts produced, after which the supernatant oil is filtered through fuller's earth filtering bed. Next, subject the filtrated oil to steam distillation in a steam still and distill off the gasoline fraction. Put the gasoline fraction in a continuous treating apparatus and wash it with sulphuric acid, alkali and water by turns. The finished gasoline thus produced has an excellent quality free from disagreeable odor.

(2) Add abietic acid of the supplemental quantity sufficient to neutralize the free alkali to the alkaline resin soap solution recovered from steam-still bottom as mentioned in the above example and saponify it. Then, add water solution of copper sulphate to the resin soap thus prepared and convert it into copper abietate. At the same time, prepared the iron salt of abietatic acid in the same manner as the above mentioned process from sodium soap of abietic acid and iron salt.

Add the solution of 140 kilograms of copper resinate in gasoline and the solution of 60 kilograms of iron resinate in gasoline at the same time to 100 kilolitres of cracked oil purified with alkali previously and refine it in substantially the same manner as the above-mentioned process.

Thus, it may be possible to obtain gasoline of superior quality which is not only free from disagreeable smell, but also has very great stability.

This invention as stated above has the following advantages:—

1. As a refining agent is brought into very intimate contact with the object to be refined easily, it can react with the whole of bad smell sources of cracked oil.

2. It is possible not only to remove disulphides produced during the reaction of this refining, but also to remove disulphides originally contained in the object to be refined by astringent and adsorptive actions.

3. For the above reason, bad smell sources can be removed completely from cracked oil.

4. As the object to be purified is not stirred or agitated, it is possible to prevent the oxidation of thioalcohols and also minimize the vaporization loss of the volatile portion of the object to be refined.

5. The recovery of refining agent is easy.

We claim:

The method of refining cracked oil, which consists in dissolving oil-soluble heavy metallic soap of abietic acid in a volatile organic solvent which will disperse homogeneously in cracked oil; pouring the solution thus obtained slowly into cracked oil while in a cold state to permit same to disperse naturally and homogeneously in the cracked oil whereby same will react with the intermingling mercaptans and precipitate same by double decomposition as insoluble metallic salts; separating the precipitate; and distilling the remaining liquor to separate it from the organic solvent.

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