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REFINING HIGHLY AROMATIC
PETROLEUM STOCKS

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The present invention relates to refining of highly aromatic petroleum stocks and, more particularly, to refining petroleum stocks containing polycyclic aromatic compounds to produce a light colored stock having color stability for a comparatively long period of time in storage.

In the catalytic cracking of petroleum highly aromatic petroleum stocks are obtained as bottoms. These highly aromatic stocks which contain as the predominant aromatic hydrocarbons such polycyclic aromatic hydrocarbons as the short chained alkyl anthracenes, phenanthrenes, fluorenes, acenaphthenes and the like do not respond satisfactorily to normal refining operations. For example, conventional acid-treating, followed by percolation through decolorizing clay, of such a stock provides a product of acceptable light color, but the oil darkens rapidly and within a few days the product becomes as dark as the original untreated stock.

It has now been discovered that such highly aromatic petroleum stocks can be treated in a novel manner to produce a light colored product which may be stored for weeks and even months without darkening. In addition to the marked improvement in the color stability of the treated oil, the treated oil has improved characteristics which make it more desirable as a plasticizer for vinyl resins. The vinyl-plasticizer produced by this novel method of refining is more compatible with vinyl resins than conventionally refined plasticizer and imparts a softness to the finished vinyl sheet that is not apparent when conventionally refined stock is employed as a plasticizer.

Water-soluble hydrohalides of nitrogenous derivatives of the polycyclic aromatic compounds present in the stock may also be recovered as an important product of the novel treatment.

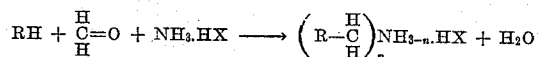
Therefore, it is an object of the present invention to provide a novel method of treating highly aromatic petroleum stock to obtain a refined oil of lighter color than that of the original stock and having color stability. It is another object of the present invention to provide a plasticizer for vinyl resins having improved color stability and improved compatibility. It is a further object of the present invention to provide nitrogenous hydrohalides of polycyclic aromatic hydrocarbons and nitrogenous derivatives of polycyclic aromatic hydrocarbons. Other objects and advantages will become apparent to those skilled in the art from the following description.

In general, the novel method of treating highly aromatic petroleum stocks to improve color and color stability comprises reacting a highly aro-

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matic petroleum stock containing polycyclic aromatic hydrocarbons such as short chained alkyl anthracenes, phenanthrenes, fluorenes, acenaphthenes and the like with an active aldehyde in the presence of a hydrohalide of ammonia, alkyl or aryl substituted ammonia, hydroxyl substituted ammonia and dialkylene substituted diamines. For example, aqueous formaldehyde, acetaldehyde, benzaldehyde and aldehydes of similar activity can be employed; in other words, aldehydes capable of participating in the Mannich reaction. Polymers of formaldehyde can be used in conjunction with a depolymerizing agent such as water or acids having a dissociation constant of at least 1×10^{-5} such as acetic acid. After the reaction has taken place, the oil may be water-washed to remove the water-soluble hydrohalides or the oil may be neutralized with aqueous caustic solution which converts the water soluble hydrohalides into oil soluble nitrogenous derivatives of the polycyclic aromatic hydrocarbons.

It is believed that the reaction with ammonium halide and the products formed from the polycyclic aromatic hydrocarbons present in the highly aromatic stocks can be represented by the following equation:



where

R is a polycyclic aryl nucleus such as that of short chain alkyl anthracenes, phenanthrenes, fluorenes, acenaphthenes and the like,

X is Cl, Br or I, and

n is 2 or 3.

Illustrative of the results produced by the novel method of treatment are the following non-limiting examples.

Example I

A highly aromatic petroleum stock having the following characteristics was treated as stated hereinafter:

A. P. I. gravity	1.2
Distillation:	
I. B. P.	° F. 574
10%	° F. 626
50%	° F. 676
90%	° F. 724
E. P.	° F. 760
Mixed aniline	° F. 72
Color	Dark
Flash point	° F. 335
Viscosity @ 100° F. seconds S. U. V.	112

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About 1236 parts by weight of the foregoing highly aromatic petroleum stock, 30 parts by weight of paraformaldehyde, 54 parts by weight of ammonium chloride and about 100 parts by weight of acetic acid were heated for about one hour at about 100° C. After cooling to ambient temperature about 200 parts by weight of water were added and sufficient isopropyl alcohol added to break the emulsion. The water layer was separated and the treated oil water-washed again and the water layer separated.

The aqueous washings were neutralized with caustic soda and 9 parts by weight of a sub-resinous amine containing 4.94 per cent nitrogen were recovered.

The treated oil was distilled under vacuum and 904 parts by weight of an oil having a boiling range of 150 to 218° C. at a pressure of 6 millimeters of mercury (310-380° C. @ 760 mm. or 580° F. to 715° F. @ 760 mm.) were recovered. This treated oil had the following characteristics:

A. P. I. gravity	4.1
Color, Lovibond	--
Viscosity @ 100° F., S. U. V. seconds	87
Mixed aniline point, ° F	59.5
Distillation:	
I. B. P., ° F	600
10%	621
50%	651
I. B. P.	734

A very viscous residue remained in the still and amounted to about 217 parts by weight and contained about 0.07 per cent nitrogen. The treated oil has been stored for 75 days without noticeable change in color.

Example II

A similar quantity of the highly aromatic petroleum stock used in Example I was treated with the same quantities of the same reactant at the same temperature. However, the treated oil was only water-washed once and then neutralized with aqueous caustic thereby ensuring that the treated oil contained some of the amines produced during treatment. Upon distillation of the neutralized treated oil a distillate was recovered having a boiling range of the untreated oil. This distillate of the treated oil contained 0.17 per cent of nitrogen. A residue representing about 10.5 per cent of the treated oil comprised higher polymeric material and contained 0.28 per cent nitrogen. Neutralization of the water-washing produced about 31 parts by weight of amines similar to those obtained in Example I.

In view of the foregoing, it is apparent that a novel method of treating highly aromatic petroleum stock, a novel treated stock of enhanced color stability, a novel treated stock containing polycyclic aromatic aminomethyl compounds, and novel polycyclic aromatic aminomethyl compounds, have been described.

We claim:

1. A method of treating highly aromatic petroleum stock constituted predominantly of polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with formaldehyde and ammonium chloride, water washing the reaction mixture and separating the water washed reaction mixture from the aqueous washings.

2. A method of treating highly aromatic petro-

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leum stock constituted predominantly of polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with formaldehyde and ammonium chloride, water washing the reaction mixture, separating the aqueous washings from the treated stock, neutralizing the water washings with alkali metal hydroxide and recovering a nitrogenous, water-insoluble product.

3. A method of treating highly aromatic petroleum stock constituted predominantly of polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with formaldehyde and ammonium chloride, neutralizing the reaction mixture with aqueous alkali metal hydroxide and separating the neutralized stock from the aqueous layer.

4. A highly aromatic petroleum stock containing polycyclic aromatic hydrocarbons and having greatly improved color stability and being more compatible with vinyl resins than a similar stock after acid refining and obtained by reacting a highly aromatic petroleum stock the components of which are practically all polycyclic aromatic hydrocarbons having alkyl chains of one and two carbon atoms with formaldehyde and ammonium chloride.

5. A highly aromatic petroleum stock containing the reaction product of polycyclic aromatic hydrocarbons, formaldehyde and ammonium chloride.

6. A method of treating highly aromatic petroleum stock constituted predominantly of polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with at least one mole of formaldehyde and at least one mole of ammonium chloride at elevated temperatures, water-washing the reaction mixture and separating the aqueous layer from the treated stock.

7. A method of treating highly aromatic petroleum stock constituted predominantly of polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with at least one mole of formaldehyde and at least one mole of ammonium chloride per average mole of said aromatic hydrocarbons at 100 degrees centigrade, neutralizing the treated stock with aqueous alkali metal hydroxide, and separating the aqueous layer from the treated stock.

8. A method of treating highly aromatic petroleum stock containing polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with an aldehyde and ammonium chloride at 100 degrees centigrade and removing unreacted aldehyde and ammonium chloride.

9. A method of treating highly aromatic pe-

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petroleum stock containing polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of petroleum containing polycyclic aromatic hydrocarbons with an aldehyde and ammonium chloride, water-washing the reaction product and separating the reaction product from the aqueous solution.

10. A method of treating highly aromatic petroleum stock containing polycyclic aromatic hydrocarbons to provide a light colored stock having greatly improved color stability which comprises reacting a highly aromatic petroleum stock obtained as bottoms in the catalytic cracking of

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petroleum containing polycyclic aromatic hydrocarbons with an aldehyde and ammonium chloride, neutralizing the reaction mixture and water-washing to remove water-soluble components of the reaction mixture.

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REFERENCES CITED

10 The following references are of record in the file of this patent:

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