The present invention has both process and composition of matter aspects. The composition of matter embodiment in its broad, general concept, comprises a major proportion of cracked petroleum fractions and a minor proportion of a particular metal-containing additive. More particularly, the composition of matter of the present invention comprises a major proportion of cracked gas oil and a minor proportion of a substituted cyclic aluminum oxide trimer of the formula:

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R
\( \text{Al} \)
```

where "R" is selected from the group consisting of acylate anions of aliphatic monocarboxylic acids containing 12 to 22 carbon atoms per molecule and alkoxyl anions of alcohols containing from 1 to 10 carbon atoms per molecule.

According to the present invention, the color stabilizing additive is prepared by admixing an aliphatic monocarboxylic acid, aluminum alkoxide, and water at a temperature of from 170°F to 250°F for a reaction time sufficient for the formation and liberation of alcohols after which time the temperature is raised to and maintained at about 350 to 360°F until further formation and liberation of alcohol ceases. The product that is formed from this reaction is the substituted cyclic aluminum oxide trimer. The substitutions will either be acylate or alkoxyl anions, depending upon the molar ratios of the reactants used. For example, if the mol ratios of acid to aluminum alkoxide to water is 1:1:1, the product will be the triacylate cyclic aluminum oxide trimer,
alcohols having substantially low volatility so that they may easily be removed by distillation from the reaction mixture. Suitable alcohols include propyl, isopropyl, butyl, amyl, and the like. The corresponding iso and secondary alcohols are also suitable. Aluminum alkoxides of mixed alcohols can also be used. It is distinctly preferred that the aluminum alkoxide be derived from isopropyl alcohol.

The hereinafter defined cyclic aluminum oxide trimer is used, according to the present invention, in amounts ranging from 0.001% to 0.1% by weight in admixture with cracked petroleum fractions. Preferably, the amount of trimer will be within the range of 0.005% and 0.01% by weight.

In the process aspects of the present invention, it was discovered that the above-defined trimer is peculiarly operable in cracked petroleum fractions which have been reduced in sulfur content by hydrorefining. Accordingly, the present invention embodies two process concepts: namely, the process of prohibiting color degradation of cracked petroleum fractions by the addition thereto of a minor amount of a substituted cyclic aluminum oxide trimer and the process of preparing a color stable furnace oil by desulfurizing cracked gas oil under hereinbelow defined operating conditions and subsequently adding thereto a minor amount of said cyclic trimer.

The process conditions necessary to effectuate proper hydrorefining of the cracked petroleum fractions include a temperature between 500°F and 675°F, preferably between 550°F and 650°F; a pressure from 300 pounds per square inch gauge to about 1000 p.s.i.g.; preferably between 500 and 800 p.s.i.g.; and a liquid hourly space velocity of from 0.5 to 10, preferably from 1 to 6.

It should be noted that the choice of operating conditions will be determined by the characteristics of the charge stock, such as boiling range, sulfur content, degree of unsaturation, and the like; the desired properties of the product, such as sulfur content, initial color, sludge formation, and the like; impurity of the hydrogen-containing gas which used, and other well-known considerations.

The term "cracked petroleum fraction" as defined herein includes any petroleum fraction of gas oil boiling range derived from thermal and/or catalytic cracking of conventional petroleum fractions. It includes those petroleum fractions, so obtained, which boil mainly between 425°F and 700°F and which contain sulfur. As used herein, the term "hydrogen" is meant any hydrogen-containing gas which is 40% to 100% free hydrogen, preferably between 70% to 100%. The hydrogen-containing gas can be mixed with inert diluents and can be derived from other refinery sources, such as reforming units. Recycle hydrogen is not required for this process.

The term "atmosphere of hydrogen" as used herein, denotes that there is no net flow of hydrogen through the contact zone other than the small amount which dissolves in the liquid effluent.

As a general embodiment of the present invention, a cracked gas oil is heated to the desired reaction temperature, for example, 600°F, and passed into a reaction zone in which it trickles downward over a sulfur-resistant catalyst. Hydrogen pressure of, for example, 650 p.s.i.g. is maintained over a liquid level in the bottom of the reactor and is admixed in an amount sufficient to make up for the hydrogen consumed in the desulfurization of the feed. This amount may vary from 25 to 300 standard cubic feet per barrel of feed stock. The reaction products are removed from the reactor and are passed to a fractionator or separator where the hydrogen sulfide and dissolved hydrogen are removed. The resulting products which are recovered from the fractionator include high-octane gasoline and a desulfurized cracked gas oil of light initial color. Usually, the octane number of the gasoline produced is within the range of 85 to 95 F-1 clear octane number, the ASTM color of the desulfurized gas oil is usually less than 1.5 and frequently is less than 1.25, and the sulfur content of the product gas oil is usually less than 0.5 weight percent.

The resulting desulfurized cracked gas oil is then mixed with, for example, 0.005 weight percent of a substituted cyclic aluminum oxide trimer comprising primarily a mixture according to the following formula:

The cracked gas oils inhibited according to the above description experienced very little degradation in color after 12 weeks of storage at 110°F.

The hydrorefining step of the present invention is carried out in the presence of a sulfur resistant hydrogeneration catalyst. Examples of suitable catalysts are metals, such as copper, zinc, mercury, vanadium, tungsten, chromium, molybdenum, manganese, cobalt, iron, nickel, platinum, etc.; oxides of such materials, or combinations of such materials and/or oxides and/or sulfides thereof. Any suitable catalyst support can be employed, for example, activated carbon, aluminum, aluminum silicate, bauxite, charcoal, clay, kieselguhr, magnesium, pumice, silica, silica alumina, mixtures of the above, and the like. The preferred catalyst is cobalt molybdate supported on alumina. When the term "cobalt molybdate" is used herein, it denotes a mixture of cobalt and molybdate oxides which may or may not be in whole or in part chemically combined.

The present invention is based on the discovery that color stabilization and substantial desulfurization of cracked gas oils is possible through a combination of critical operating conditions and a specific type of chemical additive. As for the operating conditions, the temperature employed is particularly critical. A temperature too low can impart a good initial color to the product oil but the product oil will not be susceptible to the inhibiting action of the added cyclic trimer and will not be materially desulfurized. As the temperature is increased, desulfurization is increased, and the additive response for color stability is also increased. Beyond a certain temperature, initial color darkens with increase in temperature to a point where adding the inhibitor becomes a needless act; also the sulfur removal continues to increase. Thus, there is a narrow range of temperature with which sulfur removal is substantial, initial product color is good, and additive response for color stability is acceptable. If the oil treated is relatively low in sulfur to begin with, and color improvement and color stability are the chief goals, then a wider range of temperatures may be used.

The advantages to the practice of the present invention are illustrated in the following examples which are offered in order that the invention may be more fully understood by those skilled in the art.

**EXAMPLE 1**

A catalytically cracked gas oil from Middle East crude boiling between 425°F and 625°F was contacted with a cobalt molybdate supported on an alumina catalyst in the presence of hydrogen of 100% purity with the following results:
Note that the initial color of the product increases sharply on a reactor temperature above about 625°F. Color is similarly effected. Note also that the additive response becomes negligible when a temperature of approximately 625°F is exceeded. It can be seen from this example that from this charge stock the preferred temperature is 625°F.

It is to be noted that the benefits of this invention are only obtained if the sulfur content of the cracked petroleum fraction used as a charge stock to the hydrotreating operation is at least 0.3% sulfur and the benefits are optimum if the sulfur content is greater than 1%.

**EXAMPLE II**

A catalytically cracked gas oil which had been processed according to the conditions set forth in Example I, namely the temperature of 625°F, was admixed with varying amounts of hereinabove defined cyclic aluminum oxide trimers with the following results:

<table>
<thead>
<tr>
<th>Amount of cyclic trimer as wt. percent of aluminum</th>
<th>0</th>
<th>0.005</th>
<th>0.01</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intitial: ASTN Color</td>
<td>0.25</td>
<td>0.25</td>
<td>0.28</td>
<td>0.23</td>
</tr>
<tr>
<td>Aged 12 wks, at 100°F</td>
<td>2.00</td>
<td>2.29</td>
<td>2.28</td>
<td>1.76</td>
</tr>
<tr>
<td>Filterable sludge, mg/100 mL</td>
<td>0.00</td>
<td>0.23</td>
<td>0.08</td>
<td>0.40</td>
</tr>
</tbody>
</table>

These results show a marked improvement in both color stability and reduction in sludge residue when small concentrations of the inhibitor are present. In fact, it can be seen that the amount of trimer present is critical. The concentration must be between 0.005-0.01 wt. percent of aluminum before satisfactory benefits are obtained with this charge stock. It is also to be noted that hydrogenation alone is not a satisfactory solution to the color stability problem nor to the sludge problem.

The invention claimed is:

Method for desulfurizing and increasing the color stability of sulfur-containing cracked gas oil boiling mainly within the range of 425°F and 700°F, and containing at least 0.3% sulfur which comprises (1) contacting in liquid phase said gas oil with a sulfur-resistant hydrogenation catalyst, in an atmosphere of hydrogen at a temperature of from 500°F to 650°F and a pressure of from 300 psig to 1000 psig, (2) recovering a substantially desulfurized cracked gas oil, and (3) adding to said desulfurized cracked gas oil a minor amount of a substituted cyclic aluminum oxide trimer of the formula

where "R" is selected from the group consisting of acylate anions of aliphatic monocarboxylic acids containing 12 to 22 carbon atoms per molecule and alkoxy anions of alcohols containing from 1 to 10 carbon atoms per molecule said minor proportion being an amount sufficient to inhibit color degradation of said petroleum fraction.

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