

## UNITED STATES PATENT OFFICE

2,061,111

## MANUFACTURE OF ANTI-OXIDANTS

Donald R. Stevens, Swissvale, and William A. Gruse, Wilkensburg, Pa., assignors, by mesne assignments, to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application December 13, 1933,  
Serial No. 702,258

11 Claims. (Cl. 23—239)

This invention relates to manufacture of anti-oxidants; and it comprises a process of making anti-oxidants wherein a light, cracked, petroleum distillate or a fraction obtained therefrom is reacted with an aryl hydroxy compound, the reaction sometimes taking place at elevated temperatures and usually in the presence of an acid condensing agent, and a high boiling product having anti-oxidant properties is recovered from the resulting reaction products all as more fully hereinafter set forth and as claimed.

All raw, cracked distillates made from petroleum oils whether by liquid phase processes or by the so-called vapor phase processes, contain appreciable quantities of certain constituents which deposit gum upon evaporation and, in addition, certain (probably related) constituents which deposit gum upon storage. The elimination of these constituents or obviation of their effects has presented an important problem to the petroleum industry.

These gum-forming constituents are customarily removed by chemical treatment. Of recent years a new method of preventing the deposition of gum has been developed. It has been found that small quantities of certain chemicals, when added to a motor fuel, possess the property of retarding or inhibiting the formation of gum. But many of these agents are not desirable adjuncts to a motor fuel and all of them are relatively expensive products.

The present application is a continuation in part of our copending application, Ser. No. 649,670, filed December 30, 1932, in which application we have described and claimed certain stabilized motor fuels and processes of stabilizing such fuels by adding thereto, as anti-oxidants, small amounts of the reaction products obtained by treating low boiling cracked petroleum distillates with aryl-hydroxy compounds such as phenols, the treatment being usually conducted in the presence of acid condensing agents. The present application is directed to the manufacture of the anti-oxidants used for stabilizing the motor fuels of our acknowledged application. The present case is also a continuation in part of our copending applications, Serial Nos. 591,928 and 578,412, filed February 19, 1932, and December 1, 1931, respectively. In Serial No. 591,928 we have described and claimed the refining of cracked petroleum distillates by treating the same with a mixture of sulfuric acid and a hydroxylated aromatic compound, such as a phenol; while in Serial No. 578,412 we have described and claimed the refining of cracked distillates by

treating them with anhydrous aluminum chloride and various oxygen-containing organic compounds. The present invention represents, in some respects, an improvement upon or extension of the inventions set out in the two latter acknowledged applications. It includes the recovery of certain (usually high-boiling) anti-oxidant products, obtained by treating cracked distillates by the refining processes of our acknowledged copending applications. We have found that these products possess specific anti-oxidant properties.

We have found that when light cracked petroleum distillates are reacted with aryl hydroxy compounds there are present in the reaction products certain materials which possess gum inhibiting properties in an extraordinary degree. The higher boiling products of the reaction are usually the more potent. In order to produce these gum inhibitors in high yield it is sometimes advantageous to conduct the reaction at somewhat elevated temperatures and in the presence of an acid condensing agent, such as sulfuric acid or aluminum chloride. We have found that there are certain fractions contained in cracked distillates produced according to the usual liquid phase or vapor phase processes, which appear to be particularly susceptible of reacting to produce the gum inhibiting agents of our invention. The fractions which appear to be the most active are those obtained by taking a cut to say 140° F. This may include the heavier of the hydrocarbons usually found as vapors in cracking still gases, these being sometimes called "wild" products. However, other materials including the materials produced by cracking naphtha distillates are useful in our process. In order to obtain the gum inhibiting agent in most concentrated form, we advantageously separate a low-boiling fraction from a cracked distillate, treat this low boiling fraction with an aryl hydroxy compound in the presence of an acid condensing agent, and then fractionate the resulting product by distillation, recovering high-boiling residues or distillates therefrom.

The anti-oxidant obtained by the above procedure can be made at extremely low cost. It appears to be a condensation product of the aryl hydroxy compound with certain ordinarily deleterious components of the low boiling cracked distillates. Since it is closely related in physical and chemical properties to the distillate from which it is obtained, this anti-oxidant forms an unobjectionable addition to gasoline, lubricating

oils and the like when used in the small quantities which are sufficient. Our anti-oxidant is totally soluble in gasoline and substantially insoluble in water; these being important properties of agents employed for inhibiting and retarding gum formation in motor fuels.

Our anti-oxidants are formed incidentally during the course of treating cracked distillate in accordance with the processes of our acknowledged copending applications. They occur to some extent in the cracked distillates which have been treated in accordance with these processes but they are present in greatest concentration in the residues derived from the re-running of the treated, cracked distillates. Our present invention therefore includes the recovery of anti-oxidants from the residues of the re-running step of the processes of our acknowledged copending applications.

In our acknowledged copending applications the procedure followed was adjusted to produce optimum refining of the cracked distillates treated. This exact procedure, although useful, is not necessarily the one best suited for the production of our anti-oxidants. In other words, if it is desired to produce anti-oxidants of maximum potency and in high yield, certain details of the acknowledged procedure may be varied to some extent.

We have found that cracked distillates from various sources and produced by various processes differ greatly in value as raw material for the preparation of anti-oxidants. We have tested a large number of cracked stocks and have found all of them capable of producing products having at least some anti-oxidant value. The higher boiling distillates are not as good as the lower boiling distillates.

One of the best of the low boiling distillates we have tested so far was produced by cracking a midcontinent naphtha distillate in a liquid phase cracking process at pressures of about 1500 pounds per square inch. On the other hand we have found that a so-called "cycle stock", produced by the refluxing of a cracked distillate from a Venezuela crude in a vapor phase process and having a boiling point range of from 300° to 600° F., produced anti-oxidants having relatively small potency. A high temperature, vapor phase distillate from a midcontinent crude also gave relatively poor results. This latter distillate was a highly unstable material which reacted violently with sulfuric acid. Compression plant gasolines made from pressure still and coke still gases, and the pressure still distillates from Venezuela gas oil produce excellent results.

Our anti-oxidants appear to be universally applicable for inhibiting gum formation in motor fuels. We have tested them in the stabilization of a large number of cracked distillates of different types as well as in light coal tar distillates. In all cases the formation of gum was inhibited, as determined by the copper dish and oxygen stability tests, and by actual storage tests.

As mentioned previously, it appears to be the lower-boiling fractions of the cracked distillates which react to produce the best anti-oxidants. In one operation, for example, we separated a cracked naphtha from a midcontinent stock into eight cuts and treated each fraction individually with 3 pounds of 98 per cent sulfuric acid and 10 pounds of cresylic acid, per barrel. Treatment was carried out by contacting the distillate with these chemicals at ordinary temperatures, during agitation, for a period of approximately 30

minutes. These fractions were washed with water, with alkali solution, and again with water, and then tested for anti-oxidant value.

The test employed was the usual oxygen stability test wherein a sample of gasoline, for example, is placed in a bomb under 100 pounds cold pressure of oxygen and heated to 212° F., the pressures being taken by a recording pressure gauge. In this test the time intervening between the reaching of constant pressure and the point at which the oxygen pressure shows a definite drop below the maximum reached during the test is taken as the "induction" or "oxygen stability" period. A standard gasoline, having a known induction period is usually employed, the materials to be tested for their anti-oxidant values being added in measured amount to the test sample. Any increase in the induction period of the standard is then taken as a measure of the relative anti-oxidant values of the materials added. If the heating of the bomb is interrupted after a period of 4 hours, the weight in milligrams of gum in 100 cc. of the gasoline at the end of this time is known as the "oxygen gum".

In testing the inhibitors produced from the eight cuts mentioned above, a standard gasoline having an induction period of 1¼ hours was employed. Upon the addition of 1 per cent of inhibitor from the lowest boiling cut treated, boiling up to 138° F., the induction period was increased to 16¼ hours. The inhibitors from the three fractions, boiling up to 270° F., gave induction periods ranging from 10 to 12 hours, while the inhibitor from the highest boiling cut, boiling from 326° to 395° F., gave an induction period of only 3½ hours.

While the lower boiling cracked distillates react to produce the best anti-oxidants, the active anti-oxidant principle appears to occur in the higher-boiling portions of the reaction products. Thus, when the above low boiling fraction, boiling to 138° F. was treated and then fractionated, it was found that the material boiling above 400° F. was the most effective anti-oxidant. Thus it will be seen that the anti-oxidant formed from even the low-boiling fractions of a gasoline is itself a high boiling compound.

We have found that when a cracked material treated in the manner described is distilled to recover gasoline, some of the anti-oxidant products come over with the gasoline so that this gasoline may be used for anti-oxidant purposes by blending with other less stable gasolines. The distillation of a treated product may be entirely omitted, if desired, since these products are effective anti-oxidants as a whole. It is usually better, however, when it is desired to recover substantially all the anti-oxidant values from a treated distillate and to produce a product suitable to be added directly to a finished gasoline, to distill the treated distillate as in the usual re-running operation but to carry this distillation to a considerably higher boiling point. The residues can then be discarded or otherwise disposed of.

When a cracked naphtha distillate is treated as a whole in accordance with our invention and then fractionated we have found that one of the high boiling cuts usually possesses a maximum anti-oxidant value. This cut usually has a boiling point range well above the gasoline range and, in the usual re-running operation, would normally occur in the residues or high boiling ends. In one operation, for example, we treated a cracked naphtha with 2 pounds sulfuric

acid and 6 pounds of cresylic acid per barrel. The gasoline was taken off up to about 380° F. and then the residue, amounting to about 5 per cent of the original material, was fractionated under a vacuum ranging from about 20 mm. to 5 mm. mercury. Each of the fractions was tested for anti-oxidant value, using a standard gasoline with an induction period of 1¾ hours. The results obtained were as follows:

| Fraction | Boiling points | Amount added | Stability time; |
|----------|----------------|--------------|-----------------|
|          |                | Percent      | hours           |
| 1        | 149-221° F.    | 0.01         | 4¾              |
| 2        | 221-246° F.    | 0.01         | 7               |
| 3        | 246-279° F.    | 0.01         | 11¾             |
| 4        | 279-311° F.    | 0.01         | 14              |
| 5        | 311-329° F.    | 0.01         | 10¾             |
| 6        | 329-356° F.    | 0.01         | 9½              |
| 7        | 356-401° F.    | 0.01         | 6¾              |
| 8        | Solid residue. | 0.01         | 4¾              |

It will be noted from this table that even solid residues, derived as above, possess considerable value as inhibitors.

When production of anti-oxidants is our principal desideratum, a large proportion of the aryl hydroxy compound may be used. Best results are obtained when the hydroxy compound is employed in an amount equal to or several times greater than the quantity of acid condensing agent employed. For example, when sulfuric acid is used as the condensing agent we have found that the best proportions of sulfuric acid range from about 2 to 6 pounds per barrel of cracked distillate, while the best proportions of cresylic acid, for example, to be mixed therewith range from about 2 to 12 pounds per barrel. Increasing the quantity of sulfuric acid above about 6 pounds per barrel produces no improvement and may be detrimental. The acid used should be concentrated sulfuric acid having a gravity of at least about 55° Bé. We have obtained excellent results using 2 to 3 pounds 66° Bé. sulfuric acid with 6 to 10 pounds of cresylic acid. Time of treatment may range from 5 to 60 minutes. The longer periods produce no particular benefit. The temperature of treatment may range from room temperatures up to about 180° F. Not much effect is produced by change of temperature through this range. It is usually of some advantage to heat the reaction products, say to temperatures of 400°-500° F., after washing with alkali and water. However, the temperature reached during the customary distillation or re-running is sufficient for most purposes.

It is possible to effectively combine a process of refining, in accordance with the processes described and claimed in our acknowledged copending applications, with our present process of producing anti-oxidants. Any of the processes described in our prior applications produce a certain amount of high-boiling ends during the re-running step after treatment. These high boiling ends possess anti-oxidant value. They may be recovered and added in small amount to gasoline which it is desired to stabilize. With this combined treatment, the material which would otherwise be a worthless residue becomes a highly valuable stabilizing agent.

The treated and re-run gasoline distillates obtained from our prior processes are not only highly stable but they even possess anti-oxidant properties sufficient to stabilize untreated distill-

ates when added thereto in proportions of 5 per cent or less.

When the treated distillates of our prior process are re-run as usual, but to a higher boiling point, they are much more effective as anti-oxidants than the gasoline distillates which would be obtained by customary procedure. For example the treated distillates can be distilled over in a re-running operation to boiling points ranging from about 400° to 575° F. The re-run distillates obtained in this manner are highly effective anti-oxidants. They may be used in proportions ranging from about ½ to 2 percent by weight to stabilize ordinary cracked gasolines. The proportions necessary for stabilization purposes depend upon the amount of cresylic acid, for example used during treatment. When 6 pounds cresylic acid and 2 pounds of sulfuric acid are employed, for example, 1 per cent of a distillate re-run to a boiling point of 550° F. is sufficient to stabilize most cracked gasolines. A fractional distillation to recover high boiling anti-oxidant fractions from treated distillates is not required when this procedure is followed. The re-run distillates obtained in this manner are, moreover, more effective in reducing copper dish gum than are the whole treated undistilled materials.

The stabilizing agents of our invention may be produced at practically no expense additional to that of the usual refining process. Acid treating alone applied to a specific stock produces on the average possibly 4 per cent of a high boiling residue with a specific gravity of about 0.856, having no anti-oxidant value and finding no particular use industrially. The addition of as small a quantity as 0.6 per cent by volume of cresylic acid, (based on the distillate) for example, during the treatment, produces an increase in the residue to about 5 per cent, this residue having a gravity of about 0.871. This latter residue is highly valuable as an anti-oxidant. Moreover, the latter treatment produces a gasoline which, as mentioned previously, is not only stable but which also possesses anti-oxidant value.

A certain additional quantity of anti-oxidant can be recovered from the acid sludge after treatment. If this sludge is neutralized with caustic an oily layer separates having about the same anti-oxidant value as one of the heavier cuts from the treated distillate. The aqueous layer contains substantially no anti-oxidant. This fact further corroborates the observation that the active anti-oxidant principle is oil soluble but not water soluble.

Our anti-oxidants can usually be concentrated to some extent by extraction with alcoholic potash. Thus, a distillation residue obtained by our process was extracted with alcoholic potash and the extract was then neutralized by the addition of acid. About 20 per cent of the original volume was recovered as an oily layer. This material increased the induction period of a standard gasoline from 1¾ hours to 16 hours by the addition of only 0.01 per cent by volume. The distillation residue itself, unextracted, was added to the same standard gasoline as mentioned above, in the same amount, and the so-treated gasoline had an induction period of ten hours. Extracted distillation residue was added in similar proportion to the standard gasoline mentioned above, and the so-treated gasoline had an induction period of only five hours.

A reaction between the aryl hydroxy com-

pounds and the low boiling distillates alone, without the use of condensing agents, produces a product of fair anti-oxidant value, provided heat and pressure are employed, say temperatures up to 575° F. and pressures up to 1000 pounds. When cresylic acid, for example, is added to a cracked distillate at ordinary temperatures, it produces a stabilizing effect but this is removed by an alkali wash. When the heat and pressure treatment are incorporated in the process an alkaline wash does not remove the anti-oxidant. These facts show that a new chemical compound has been formed, presumably by a reaction between the cresylic acid and certain unstable compounds contained in the cracked distillate. A gasoline stabilized by our process, using mixtures of cresylic and sulfuric acids, shows no change in stability after a thorough alkaline wash. This is because the anti-oxidant is substantially insoluble in aqueous caustic solutions. Presumably the action of the sulfuric acid as a condensing agent has the same effect as the use of heat and pressure.

The anti-oxidant produced in accordance with our invention, using cresylic and sulfuric acids, is considerably more potent than cresylic acid itself and a much larger quantity of anti-oxidant is obtained than the amount of cresylic acid used in the process. This shows that some other anti-oxidant is actually produced during the process.

In reference to the question as to which organic compounds are capable of use in producing our anti-oxidants, it may be said that aryl hydroxy compounds in general appear operative. The presence of such groups as nitro, carboxylic, carbonyl, cyanide and halogen, are usually deleterious, while alkoxy, sulfonic and hydrocarbon substituents of all types, such as alkyl and aralkyl groups, do not appreciably impair the effectiveness of the compounds and may be advantageous. Among the compounds with which we have had the greatest success, there may be mentioned various phenols, both mono and polyhydric, together with their homologues such as the cresols, various naphthols, anthrols, xylenols, isopropyl cresols, resorcinol, butyl cresol, etc. Phenolic and aromatic alcoholic compounds in general appear applicable where-in the hydroxy group represents the chief function of the compound. Some of the cheapest of these materials with which we have had success in practical operation are the various "tar acids" of commerce and their fractions. These are crude products obtained by dephenolizing gases from by-product coke oven operation and by the distilling of coal tar itself, and contain varying proportions of phenols and cresols, together with some xylenols and various hydrocarbons. These tar acids are usually known as "cresylic acid".

Any of the usual acid condensing agents can be employed in connection with the above aryl hydroxy compounds. The agents with which we have had most success include sulfuric acid and anhydrous aluminum chloride. Other materials such as hydrogen chloride, ferric chloride and boron tri-fluoride may be used. In addition we have found that the sulfuric acid used in treating may be re-used with entirely satisfactory results. Where an excess of phenolic compound has been used, it may be recovered by known methods.

Our invention can be more readily explained by reference to the following specific examples

which represent practical embodiments thereof.

*Example 1.*—A naphtha distillate from a pressure cracking still was treated at ordinary temperatures with a mixture of 2 pounds sulfuric acid and 6 pounds of cresylic acid per barrel. The acid sludge was settled out and the reaction product (i. e. the treated naphtha) was washed with alkali and with water and then distilled with fire to 385° F. The residue was introduced into a vacuum still, operating at about 9 mm. pressure, where it was fractionated into 3 cuts. The first cut, representing about 42 per cent was found to have the best anti-oxidant characteristics. When 0.01 per cent of this was introduced into a standard gasoline having an induction period of 1¼ hours, this period was increased to 14¼ hours. When 0.02 per cent of this anti-oxidant was introduced into a finished, untreated gasoline, it was found to produce a degree of stability sufficient for all purposes.

*Example 2.*—A naphtha distillate from a pressure cracking still was re-run at atmospheric pressure and was then cut to 138° F. The low-boiling fraction thus obtained was treated at ordinary temperatures with a mixture of 3 pounds sulfuric and 10 pounds cresylic acid per barrel. The reaction products of this treating process were freed of acid sludge, washed with alkali to remove acid residues and were then distilled with fire to 400° F. The residuum from this distillation was found to have a high anti-oxidant value, increasing the induction period of a standard gasoline from 1¾ hours to 11½ hours. 0.01 per cent of this product was added to a finished, treated gasoline for stabilization purposes.

In order to produce an anti-oxidant of maximum potency it is only necessary to fractionate a residuum obtained as above and to select a cut boiling between about 250° and 350° F. under 10 to 15 mm. pressure.

*Example 3.*—A distillate produced by cracking a naphtha (naphtha cracker distillate) was treated with 2 pounds sulfuric acid and 2 pounds cresylic acid per barrel. The reaction products of this treating process were freed of acid sludge, washed with alkali to remove acid residues and were then fractionated. Two cuts boiling from 70°–218° and 218°–272° F. were found about equal in anti-oxidant value. In concentrations of 2 per cent these cuts raised the induction period of a standard gasoline from 1¾ hours to 2¾ hours. The higher boiling cuts were considerably more potent. The cut boiling between temperatures of 400° and 510° F. for example, was found to increase the induction period of the standard gasoline to a value of 9½ hours when added in concentrations of only 0.01 per cent. The residue, after taking the last mentioned cut, gave a corresponding value of 8¾ hours.

The 400° to 510° F. cut, was found capable of stabilizing an untreated gasoline when added thereto in concentrations of 0.03 per cent.

Naphtha cracker distillates in general appear to be effective for producing potent anti-oxidants. By "naphtha cracker distillates" we mean pressure distillates boiling up to, say 410° F.; these distillates being more unsaturated than ordinary pressure still distillates but somewhat less saturated than vapor phase distillates. They are made by cracking heavy paraffinic naphthas having boiling points of about 300° to 450° F., cracking being under pressures of the order of 1500 pounds and at temperatures of about 950° F.

*Example 4.*—A naphtha distillate from a pres-

sure cracking still was treated with 1 per cent of anhydrous aluminum chlorid and a proportion of phenol equi-molecular to the amount of aluminum chlorid; treatment being conducted at a temperature of about 185° F. The aluminum chloride sludge was settled off and the treated naphtha was then washed with alkali and water. The naphtha was fractionated to recover gasoline. A fraction of the residue, taken between the temperatures of 440°-570° F., was found to have anti-oxidant properties, sufficient to raise the induction period of a standard gasoline from 1¾ hours to 4½ hours upon the addition of 0.01 per cent. 0.05 per cent of this product was added to a finished gasoline for stabilization purposes.

One highly effective method of employing our anti-oxidants is in connection with any of the usual so-called inhibiting agents. We have discovered, surprisingly, that the copper dish gum of cracked gasolines is lowered by a combination of our agents with other inhibiting agents to a greater extent than can be usually accomplished by the use of either agent alone. This is shown by the following table which gives certain stability data obtained after adding the stated amounts of inhibitors to a base gasoline representing a mixture of pressure still distillate 35 per cent, naphtha cracker distillate 35 per cent and straight run gasoline 30 per cent; this base gasoline having a copper dish gum of 273 and an oxygen stability period of 3 hours.

| Inhibitor                                 | Amount added | Copper dish gum | Oxygen stability period |
|-------------------------------------------|--------------|-----------------|-------------------------|
|                                           | Percent      |                 | Hours                   |
| Alpha naphthol.....                       | 0.001        | 235             | 3¼                      |
| Alpha naphthol.....                       | 0.002        | 141             | 7½                      |
| Inhibitor A.....                          | 1            | 60              | 7½                      |
| Inhibitor A (1%) plus alpha naphthol..... | 0.002        | 17              | 10¼                     |

Inhibitor A in the above table represents an anti-oxidant produced by treating a whole naphtha cracker distillate with 2 pounds sulfuric acid and 6 pounds cresylic acid per barrel, separating acid sludge, washing with water and alkali and then distilling to a cut at 550° F. Results analogous to the above were obtained upon similarly testing a large number of other commercially used inhibitors, such as a mixture of alpha naphthol and alpha naphthylamine, for example.

In employing our anti-oxidants in connection with other inhibiting agents it is advantageous to employ both agents in small amounts, in themselves insufficient to produce the desired stability but sufficient in combination. Merely increasing the amount of either agent alone does not ordinarily produce as good results as the combination. The peculiar effectiveness of the combination of anti-oxidants is especially noticeable upon the copper dish gum.

While the above specific examples represent certain advantageous embodiments of our invention, it is evident from the preceding discussion that these examples could be multiplied almost indefinitely without departing from the scope of our invention. While we have mentioned our new anti-oxidants only in connection with the stabilization of motor fuels, they are useful for a large number of allied uses.

Our new products may be used as anti-oxidants for all industrial purposes wherein materials of this nature are beneficial. They may be used for stabilizing kerosene, lubricating and trans-

former oils. They form a valuable addition to rubber for prevention of ageing. They are capable of stabilizing fatty oils, such as the red oil used for textile purposes. They are also useful for preserving the value of pyrethrum fly sprays.

Another specific purpose for which our anti-oxidants are adapted is the elimination of gum formation in manufactured and coke oven gases. We have found that our products can be introduced into such gases by the so-called vaporization or fogging method, usually used for adding light lubricating oils or gas oils to these gases, the latter oils being introduced to keep lines moist and meter leathers in good condition. When our anti-oxidants are employed it has been found that gum formation is eliminated in the gas lines. Moreover, our anti-oxidants have been found to perform the same functions as the petroleum oils. Hence, when our anti-oxidants are added to prevent gum formation, the customary use of petroleum oils can sometimes be eliminated.

Most of the properties of our anti-oxidants have been set out previously. To summarize, they are reaction or condensation products of low-boiling cracked petroleum distillates and aryl hydroxy compounds. They are oily products, substantially insoluble in water and in aqueous alkali solutions, but soluble in oils and usually capable of concentration by extraction with alcoholic alkali solutions. Our higher boiling and solid products are of the nature of resins. The products having maximum anti-oxidant potency have boiling points at atmospheric pressure roughly between about 375° and 600° F., this boiling point range varying to some extent with the aryl hydroxy compound used in their preparation. They are capable of stabilizing finished gasolines when used in amounts ranging from about 0.005 to 2.5 per cent by volume, depending of course upon the type of gasoline to be stabilized.

While our invention has been set forth in some detail, various modifications in the procedures outlined may be made without departing from the spirit of our invention. Such modifications as fall within the scope of the following claims will be immediately evident to those skilled in the art.

What we claim is:

1. A process of making antioxidants which comprises treating a cracked petroleum distillate with a mixture of a phenol and sulfuric acid in proportions ranging from about 2 to 6 pounds of sulfuric acid and 2 to 12 pounds of the said phenol to one barrel of cracked distillate, said treatment being conducted at ordinary temperatures, freeing the reaction mixture of acid sludge formed during reaction, washing the sludge-free mixture with an aqueous alkali solution and fractionally distilling the alkali washed mixture to recover a fraction distilling between 365° and 600° F.

2. A process of making antioxidants which comprises reacting a cracked petroleum distillate with a phenol in the presence of sulfuric acid, washing the reaction mixture with an aqueous alkali solution, distilling the washed mixture to recover a fraction boiling in the gasoline range, extracting the distillation residue with an alcoholic solution of alkali, neutralizing the extract with acid and recovering the product separating therefrom after neutralization.

3. A process of making antioxidants which comprises treating a cracked petroleum distillate with a small amount of an acid condensing agent and a phenol at ordinary temperatures, washing the treated distillate with an aqueous alkali solution, redistilling the washed distillate to recover a gasoline fraction, extracting the distillation resi-

due with an alcoholic alkali solution, neutralizing the extract with acid and recovering the oily product thereby separated.

4. A process of making anti-oxidants which comprises treating a cracked petroleum distillate with a mixture of a phenol and sulfuric acid in proportions ranging from about 2 to 6 pounds of sulfuric acid and 2 to 12 pounds of said phenol to one barrel of cracked distillate, said treatment being conducted at ordinary temperatures, freeing the reaction mixture of acid sludge formed during reaction, washing the sludge-free mixture with an aqueous alkali solution and recovering the alkali-washed product.

5. A process of making anti-oxidants which comprises treating a cracked petroleum distillate with a mixture of a phenol and an acid condensing agent, proportions of phenol and acid condensing agent being respectively less than 6 percent and less than 3 percent by weight of the cracked distillate, said treatment being conducted at ordinary temperatures, freeing the reaction mixture of acid sludge formed during reaction, washing the sludge-free mixture with an aqueous alkali solution, fractionally distilling the alkali-washed mixture and recovering a fraction distilling between 365° and 600° F.

6. The process of claim 5 wherein said acid condensing agent is aluminum chloride.

7. A process of making anti-oxidants which comprises reacting, in the presence of an acid condensing agent, a cracked petroleum distillate with a phenol, removing residues of said acid condensing agent and unreacted phenol from the re-

action mixture by washing with an aqueous alkali solution, distilling the washed reaction mixture to a boiling point ranging from about 400 to 575° F. and recovering the distillate.

8. In the manufacture of anti-oxidants, the process which comprises reacting a cracked petroleum distillate with a phenol at a temperature of about 575° F. and at a pressure of about 1000 lbs. per square inch in the absence of an acid condensation catalyst.

9. In the manufacture of anti-oxidants, the process which comprises reacting a cracked petroleum distillate with cresylic acid at a temperature of about 575° F. and at a pressure of about 1000 lbs. per square inch in the absence of an acid condensation catalyst.

10. In the manufacture of anti-oxidants, the process which comprises reacting a cracked petroleum distillate with a phenol at a temperature of about 575° F. and at a pressure of about 1000 lbs. per square inch in the absence of an acid condensation catalyst, washing the reaction product with aqueous alkali solution and recovering the washed reaction product.

11. In the manufacture of anti-oxidants, the process which comprises reacting a cracked petroleum distillate with cresylic acid at a temperature of about 575° F. and at a pressure of about 1000 lbs. per square inch in the absence of an acid condensation catalyst, washing the reaction product with an aqueous alkali solution and recovering the washed reaction product.

DONALD R. STEVENS.  
WILLIAM A. GRUSE.