

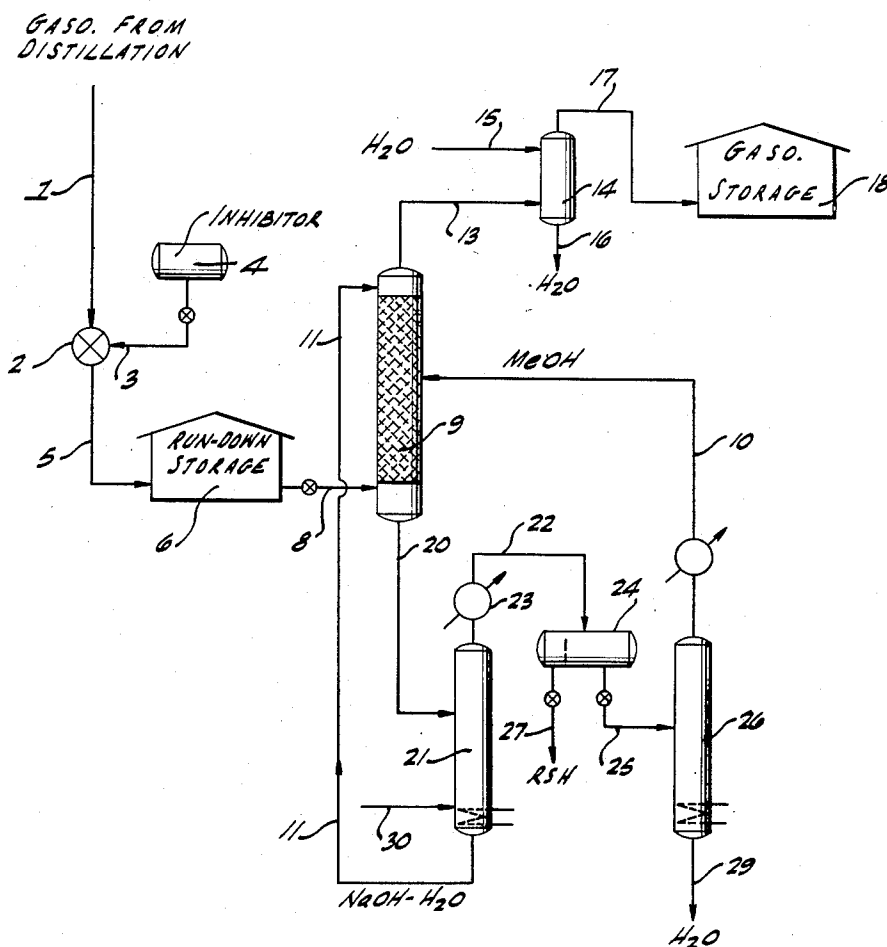
**May 20, 1958**

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**2,835,564**

# PROCESS FOR SWEETENING AND STABILIZING CRACKED GASOLINES

Filed June 25, 1956



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1

2,835,564

PROCESS FOR SWEETENING AND STABILIZING  
CRACKED GASOLINES

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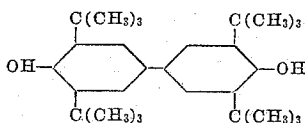
Application June 25, 1956, Serial No. 593,631

2 Claims. (Cl. 44-78)

This invention relates to methods for sweetening cracked gasolines, i. e. removing mercaptans, while also preventing oxidative changes normally resulting in gum formation. The sweetening methods employed herein comprise the aqueous caustic, or caustic methanol-water, extraction procedures which are per se well-known in the art. These caustic sweetening methods however do not effect stabilization of such gasolines, and will sometimes accelerate gum formation. According to the present invention, a novel inhibitor is added to the gasoline prior to caustic washing, whereby peroxidation may be prevented before, during, and following the caustic scrubbing operation, to a greater degree than has been heretofore possible.

The use of phenolic inhibitors for preventing oxidation of cracked gasolines is well-known in the art. However, the majority of such phenolic compounds are soluble in caustic solutions, and especially in caustic methanol-water. Hence, such phenolic inhibitors can only be added to the gasoline following the caustic washing treatment. This is disadvantageous because it is frequently desirable to store the gasoline for considerable periods of time prior to the caustic washing treatment. Moreover, in the caustic treatment itself, air is ordinarily not excluded from the scrubbing tower, and the presence of air and caustic tends to accelerate the formation of peroxides and gums in the gasoline. It would hence be highly desirable to add the inhibitor to the gasoline immediately following the run-down of gasoline from the distillation column, and in any event prior to the caustic washing treatment.

One of the most widely used phenolic inhibitors is 2,6-di-tert-butyl-p-cresol. This material is an active stabilizer, and possesses a fair degree of insolubility in caustic solutions. However, I have now discovered an even more effective, and caustic insoluble, phenolic stabilizer. This material consists of the novel compound 3,3',5,5'-tetra-(tert-butyl)-4,4'-dihydroxy diphenyl, having the structural formula:



It is accordingly the principal object of this invention to provide methods for effecting caustic washing of cracked gasolines in the presence of a highly effective oxidation inhibitor. A further object is to provide a phenolic oxidation inhibitor which is insoluble in aqueous caustic, and in caustic methanol-water, and which may therefore be added to the gasoline prior to caustic treatment. Another object is to provide a phenolic inhibitor of higher potency than has heretofore been available. Other objects will appear from the following description.

U. S. Patent No. 2,479,948 discloses a class of inhibitors which may be designated as 3,3',5,5'-tetra-alkyl-4,4'-dihydroxy diphenyls, wherein not more than two of the

2

alkyl groups are tertiary alkyl groups. The compound 3,3',5,5'-tetra-tert-amyl-4,4'-dihydroxy diphenyl is disclosed therein, but is shown to be ineffective as an inhibitor, being less active than ordinary cresylic acids.

The other compounds disclosed, which contain primary and/or secondary alkyl groups, while stated to be relatively active as inhibitors, are appreciably soluble in alkaline solutions. The present invention embodies my discovery that the specific compound 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl is highly active as an inhibitor and is also very insoluble in alkaline solutions. This novel compound is in fact more active than any other known dihydroxy diphenyl inhibitor, and is also more active than di-tert-butyl p-cresol.

The accompanying drawing illustrates schematically one method of practicing the invention, but is not intended to be limiting in scope.

The cracked gasoline from the initial distillation is brought in through line 1, and admixed in mixing valve 2 with inhibitor added via line 3 from storage tank 4. The inhibitor may be added in the solid state, or it may be added as a concentrated solution in benzene or other hydrocarbon, acetone, or other oil-miscible compound. The proportion of inhibitor to be added should range between about 0.001%–0.2% by weight, although any minor proportion is effective in some degree. The gasoline containing the inhibitor is then transferred via line 5 to run-down storage tank 6, where it may be stored for any desired length of time, prior to caustic washing.

As the stabilized gasoline is desired for caustic treatment, it is withdrawn through line 8 and transferred to the bottom of caustic scrubbing column 9, which may be any conventional type for effecting countercurrent liquid-liquid extraction, e. g. a column packed with glass beads, porcelain chips or the like. In column 9 the gasoline flows upwardly, and contacts descending caustic methanol-water, which effects extraction of substantially all of the mercaptans, but does not extract any significant proportion of the inhibitor. In the preferred operation, recycle methanol is added at a mid-point in the column via line 10, while aqueous caustic is admitted at a higher point in the column via line 11. In this manner any dissolved or entrained methanol in the gasoline is removed between the inlet points of lines 10 and 11. The resulting gasoline withdrawn through line 13 is substantially free of mercaptans and methanol, but may contain traces of dispersed caustic solution, and hence may be scrubbed in column 14, countercurrently to water admitted through line 15. Spent wash water is withdrawn through line 16. The final gasoline is withdrawn through line 17 and sent to storage indicated at 18. The gasoline in storage tank 18 still contains substantially the same amount of inhibitor as was added at mixing valve 2, and may hence be stored indefinitely while obtaining the full effects of the inhibitor.

The spent mixture of methanol, water, caustic and dissolved mercaptides is withdrawn from column 9 through line 20 and sent for regeneration to a stripping column 21. In this column, which is maintained at a bottoms temperature between about 100° and 250° C., the mercaptides are substantially completely hydrolyzed, and a mixture of free mercaptans, methanol, and water is distilled overhead. This mixture is then condensed in cooler 23 and sent to a decanter 24 via line 22. Liquid mercaptans form a supernatant phase which is removed via line 27, and may be subsequently treated for the recovery of the mercaptans by methods forming no part of the present invention.

The lower layer of methanol and water in decanter 24 is withdrawn via line 25 and sent to a methanol recovery column 26 wherein methanol is distilled overhead and recycled via line 10 to a mid-point of caustic scrub-

bing column 9, as previously described. The aqueous bottoms from column 26 is withdrawn through line 29 and may be discarded if desired. In order to make up for the loss of water in column 26, it is usually desirable to inject steam into stripping column 21 via line 30.

The aqueous caustic which is recycled through line 11 preferably consists of sodium hydroxide containing between about 20-40% by weight of NaOH. If potassium hydroxide is employed a somewhat higher proportion is preferable, e. g. 25-60 weight-percent. The methanol recycled via line 10 may be substantially anhydrous, or the distillation in column 26 may be operated to obtain a rougher separation, whereby some water returns via line 10. The volume of methanol recycled via line 10 should preferably correspond to about 10-40 volumes per 100 volumes of aqueous caustic recycled via line 11. Caustic extraction column 9 is ordinarily operated at substantially atmospheric temperatures, but any temperature between about 50°-150° F. may be employed. Under these conditions it is found that substantially none of the inhibitor is removed from the gasoline stream passing through extraction column 9.

While the above illustration shows the use of methanol-containing caustic, other caustic treating solutions may be employed. In the treatment of light naphthas, especially those containing only small amounts of mercaptan sulfur, the methanol may be unnecessary. Lower mercaptans are sufficiently soluble in aqueous caustic alone. However for stocks containing appreciable quantities of higher mercaptans, the use of a solutizer such as methanol is usually desirable. Other solutizers include ethanol, isopropanol, cresols, acetone and the like.

The compound 3,3',5,5'-tetramethyl-4,4'-dihydroxy diphenyl is substantially soluble in 10% aqueous sodium hydroxide, and is hence not usable in the present invention. The compounds, 3,3'-dimethyl-5,5'-di(tert-butyl)-4,4'-dihydroxy diphenyl, and 3,3',5,5'-tetra-isopropyl-4,4'-dihydroxy diphenyl, are slightly soluble in 10% sodium hydroxide, and are substantially soluble in caustic alcohol, and are hence not usable herein. The compound, 3,3',5,5'-tetra(tert-amyl)-4,4'-dihydroxy diphenyl is insoluble in all caustic solutions, but is only about one-tenth as active as the tetra-tert-butyl compound. Only the tetra-tert-butyl compound appears to possess the desired combination of caustic insolubility and activity which is essential herein.

The novel inhibitor of this invention may be prepared by the methods described in U. S. Patent No. 2,479,948, or preferably by the method described in my copending application Serial No. 269,891, filed February 4, 1952, now U. S. Patent No. 2,785,188. In the latter method, a 2,6-di-tert-butyl-4-halophenol is treated with a mild oxidizing agent such as air, in the presence of a copper catalyst and an alkaline material, whereby there is formed 3,3'-5,5'-tetra-tert-butyl-4,4'-diphenylquinone. The diphenylquinone is then subjected to mild hydrogenation, as for example by means of zinc dust and acetic acid, to form the diphenol.

The potency of gasoline stabilizers may be evaluated by means of peroxide number determinations. In this procedure, the gasoline sample is exposed to air for varying lengths of time, and is then titrated with a reducing solution consisting essentially of 0.01 N-titanous chloride, in order to determine the peroxide content, and thus the amount of oxygen taken up. This method is more particularly described in U. O. P. Laboratory Test

Methods for Petroleum and its Products, Universal Oil Company (1940).

#### Example

In order to evaluate the stabilizing activity of the inhibitor of this invention, peroxide numbers were determined for three samples, A, B, and C, of a light cracked gasoline boiling between 100°-300° F., and derived from a California crude oil. Sample A contained no inhibitor; sample B contained 0.0035% of 2,6-di-tert-butyl p-cresol; and sample C contained 0.0035% of 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl. The results were as follows:

| Sample | Peroxide No.                    |                                 |                                |
|--------|---------------------------------|---------------------------------|--------------------------------|
|        | After 24 hours' exposure to air | After 72 hours' exposure to air | After 17 days' exposure to air |
| A----- | 0.9                             | 4.3                             | -----                          |
| B----- | 0.03                            | 0.05                            | 0.13                           |
| C----- | 0.03                            | 0.03                            | 0.08                           |

This data shows that 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl is effective in extremely small amounts for preventing the formation of peroxides in cracked gasolines, and that it retains its activity for a longer period of time than does 2,6-di-tert-butyl p-cresol. Inasmuch as these peroxides are considered to be precursors of, or essential factors in, the formation of gums in gasolines, it is clear that the above compound is a highly effective stabilizer.

When the procedure employed for testing sample C is repeated, following 10 minutes of shaking the gasoline sample with a caustic solution composed of 100 volumes of 20% aqueous NaOH solution to which 20 volumes of methanol has been added, the peroxide numbers of the caustic-washed gasoline after 24 hours, 72 hours and 17 days exposure to air are substantially the same, respectively, as indicated above. No detectable amounts of inhibitor are present in the caustic solution.

The foregoing disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A method for stabilizing and sweetening a cracked gasoline which comprises first dissolving in said gasoline a minor proportion, less than about 0.2%, of 3,3',5,5'-tetra(tert-butyl)-4,4'-dihydroxy diphenyl, then subjecting said gasoline to caustic extraction with a caustic solution to extract mercaptans without extracting substantial proportions of said inhibitor, said caustic solution consisting of an alkali metal hydroxide dissolved in a solvent which is predominantly water.

2. A process as defined in claim 1 wherein said caustic solution is a caustic methanol-water solution containing between about 10 and 40 volumes of methanol dissolved in 100 volumes of an aqueous caustic solution, said aqueous caustic solution containing between about 20% and 40% by weight of NaOH.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

2,479,948 Luten et al. ----- Aug. 23, 1949  
2,616,831 Rosenwald ----- Nov. 4, 1952