

## UNITED STATES PATENT OFFICE

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## TREATMENT OF INHIBITORS

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This invention relates to the treatment of inhibitors and refers more particularly to the treatment of a certain class of inhibitors which have been found to be of special value when used in cracked gasolines to prevent the development of undesirable properties therein during storage.

More specifically the invention has reference to treatment of wood tars or fractions thereof which represent a class of semi-refined inhibiting materials which are cheap and easily procurable and which have equal or better inhibiting value than the majority of individual chemical compounds used for inhibiting purposes. The present invention is particularly directed to the purification and improvement of tars and fractions thereof produced from the distillation of various types of wood, although it is also applicable to the treatment of other heavy tars such as those produced from coal, lignite, etc.

20 The value of wood tar fractions as inhibitors of gum formation, color depreciation and loss in antiknock value is affected by a number of factors such as, for example, the readiness with which the gasoline to be inhibited oxidizes and 25 polymerizes under average storage conditions and on the side of the wood tar itself by the source, type and age of the wood distilled and the conditions of distillation such as, for example, the use of steam or vacuum and in the soft woods by the removal of its resinous materials 30 by solvent extraction prior to its distillation in some cases.

While crude wood tars as produced in the primary distillation of various woods are all 35 serviceable to some extent as inhibitors in unstable gasolines, experience has shown that it is preferable to use selected intermediate cuts for several reasons. In the first place, the lower boiling fractions, say those boiling below 425—464° F., have generally a considerably lower inhibiting potency than those boiling within the range of 464—572° F., and particularly those boiling between 464—536° F., the last fraction named being particularly efficient in practically all 45 cases. The lower boiling fractions are at the present time practically never utilized as inhibitors on account of the excessive quantities required to effect stabilization and the fractions boiling above 572° F. contain such quantities of 50 heavy pitches that their use is precluded on account of the effect which the requisite quantities have on the color, color stability and translucency of the gasoline. During storage of wood tars or their fractions there is frequently a development of relatively high boiling pitchy ma-

terials which lower the value of the wood tar cut when used in gasoline.

In one specific embodiment the present invention comprises the treatment of wood tars or fractions thereof intended for use as inhibitors in gasoline by polymerizing agents comprising heavy metal salts, treatments being conducted in either liquid or vapor phase.

The preferred treating materials according to the process of the present invention comprise such compounds as the halides, and particularly the chlorides of such metals as aluminum, zinc, tin, iron, etc., which have known value as reagents for effecting polymerization or condensation reactions. The sulphates of these metals and other inorganic salts may sometimes be used in lieu of the preferred halides. While the alternative use of different salts of this character is comprised within the scope of the invention, it is not to be assumed that they will be equivalents in their action upon different wood tar fractions under conditions of treatment which may be varied to produce the desired refining with maximum efficiency.

20 The reactions produced upon wood tar fractions by the use of the preferred treating materials are in general those of polymerization and/or condensation among the molecules of the constituent compounds. It is observable that there is a general elevation of the boiling point 25 curve, and it has been found that the percentage yield of the intermediate fractions most serviceable as inhibiting material is practically always increased. Thus, on the one hand, fractions boiling below 425° F., for example, are converted to a substantial extent into fractions boiling between 30 425—572° F., while the less effective constituents of the 425—572° F. fraction are polymerized to 35 heavy pitches, which are eliminated during a subsequent distillation.

When treating different wood tar fractions in liquid phase the viscosity of heavy cuts may be reduced by the use of solvents to produce a fluid which is more readily contacted with the polymerizing agents and from which the polymerized materials are more readily separable either by settling or filtering. This dilution or cutting back of the tar while not a special feature of the invention is generally preferable in liquid phase treatments. In such cases after the treatment is effected the subsequent distillation removes the solvent as a primary light cut and the desired treated wood tar fraction as an intermediate or heart cut and leaves the heavy asphaltic polymers as a residue.

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The polymerizing salts may be used either as solids or in solution. Such salts as aluminum chloride are best used in anhydrous condition and in liquid phase treatments the pulverized 5 salt may be mechanically agitated with a cut-back wood tar fraction in small quantities. Ferric chloride may be used in a similar manner or in solution, while the chlorides of zinc and tin may be employed in solutions of controlled 10 concentration usually approaching saturation. The amounts of these reagents necessary for effective treatments will vary with their inherent polymerizing power and the degree of treatment most desirable on the particular fractions of wood tar 15 undergoing treatment, though the amounts are usually small and the process is thus economical.

As a rule the amount of reagent employed, calculated on the basis of the anhydrous salt, seldom exceeds 5 per cent by weight of the wood tar 20 fraction treated. From this figure the amounts used may range down to as low as 0.5 per cent, as will be shown in subsequent examples. When treating the lower boiling range wood tar fractions (those boiling below 425° F.), larger quantities 25 of the reagents may be employed, while in the treatment of intermediate boiling range fractions to eliminate heavy pitchy materials, the lower amounts of reagents will be used.

In liquid phase treatments the wood tar or 30 fraction thereof is usually refluxed with the reagent for a time sufficient to bring about the desired conversion. Generally a redistilling step is necessary for the complete removal of heavy pitches and other reaction products of a complicated character, including metallo-organic addition 35 complexes, and it may be conducted under varying pressures at different stages, that is in removing any light solvent which may have been employed, atmospheric pressure may be satisfactory while reduced pressures corresponding to a high degree of vacuum may produce the best results in the recovery of the treated tar fraction 40 as a heart cut.

As an alternative mode of treatment the 45 vapors of a wood tar or fraction thereof may be treated when under a considerable vacuum corresponding generally to less than 10 mm. of mercury so that the vapor temperature is kept low. As a general rule unless this point is observed the 50 reactions of polymerization take place to too great an extent, causing undue loss of material and sometimes loss of inhibiting value in recovered fractions.

In conducting vapor phase treatments the tar 55 fractions to be treated are distilled either from batch or continuous stills and contacted with polymerizing salts in treaters which may either contain composite contact masses comprising relatively inert materials containing regulated amounts 60 of polymerizing salts or which may function as fractionators, in which case solutions of salts, such as for example zinc chloride, may be passed counterflow to the vapors. In the latter case the tower may contain filling material such as regularly spaced pans or trays of some character or 65 may be filled with silica fragments, Raschig rings or some other form of filler adapted to break up the streams of solution and cause closer contact with the vapors. The concentration of the solutions employed to effect the vapor phase treatment 70 will approach saturation and may be maintained by the presence of steam in the vapors to prevent undue concentration of the solution and consequent separation of the solute.

75 As an alternative mode of vapor phase treat-

ment such salts as aluminum chloride may be introduced into the vapors in vapor form and substantially anhydrous condition or concentrated solutions of other salts not subject to extensive hydrolysis may be injected or atomized into the vapor stream. The separation of polymers and sludge products needs no special description as this may be accomplished by any common means.

The treated vapors may be fractionated if desired either under vacuum or under normal pressures, although as a rule the easiest mode of operation is to maintain vacuum through the fractionator and in the receiver for finished product by withdrawing fixed gases from the receiver at the necessary rate.

The following examples of the practical value of the present process are given as illustrative, though the invention is not considered to be unduly limited by the particular data presented.

#### Example 1

In this instance a hardwood tar having 55.3 per cent by volume boiling within the range of 356-425° F. and 31.7 per cent by volume boiling between 425-572° F., was taken for treatment. The inhibiting value of the light and intermediate fractions was taken as proportional to the increase in induction period in the currently used oxygen bomb test produced by the addition of 0.05 per cent of the fraction to a paraffinic cracked gasoline. In the case of the lower boiling fraction the increase in the time to measurable oxygen absorption was 300 minutes, while that produced by the heavier fraction mentioned was 970 minutes.

The whole wood tar containing the fractions mentioned was treated with 5 per cent by weight of the powdered zinc chloride at a temperature of about 250° F. and atmospheric pressure. The products of this reaction were subjected to a vacuum distillation and it was then found that the percentage of material boiling below 425° F. had been reduced to 30 per cent of the whole tar, while the fraction boiling between 425-572° F. had been increased to 48 per cent on the same basis. The inhibiting values measured by the induction periods were 440 and 1300 minutes, respectively. The remaining portions of the tar were left in the distillation retort as a heavy pitch.

Both fractions were found to have a much lighter color than the corresponding boiling range cuts from the original tar and improved color stability.

#### Example 2

In this case a low boiling fraction constituting 45 per cent of another wood tar and boiling below 425° F. was treated with about 3 per cent by weight of anhydrous aluminum chloride at the same temperature as in Example 1. The low boiling fraction before treatment increased the induction period of the paraffinic cracked gasoline by about 300 minutes when used in an amount of 0.02 per cent by weight of the gasoline. As a result of the treatment and the subsequent distillation, the boiling range of the fraction was increased so that 60 per cent boiled within the range of 425-572° F., and the induction period increase produced by 0.02 per cent by weight of the whole treated fraction, constituting 90 per cent of the original, was 900 minutes. Again both color and color stability were improved.

## Example 3

When adding a fresh tar fraction boiling between 425-536° F. to a gasoline of 30 color on the Saybolt scale in amounts of 0.05 per cent the color was affected but little so that the drop was only to 29 on the Saybolt scale. However, after storage of the tar for a period of several months the effect of the addition of the required amount to various gasolines was to lower the color to approximately 25 and to produce in addition a slight but definite haze in the gasoline which was undesirable from a sales standpoint.

Such an aged tar fraction diluted with a light gasoline was then treated with approximately 5 per cent of a substantially saturated zinc chloride solution, and when redistilled to remove solvent and residual products, using vacuum as the wood tar fraction distilled, it was found that the original valuable properties of the wood tar had been entirely restored with only minor losses in volume, less than 5 per cent. It was also found that the color stability of the gasoline was better after the addition of the required amount of treated wood tar. The general results of the treatment may be summarized in the following table showing the results with cracked gasolines from different charging stocks.

## Color and color stability of uninhibited and inhibited gasoline

	No inhibitor	Fresh inhibitor	Aged inhibitor	Treated inhibitor	
35 Inhibitor, per cent.	-----	0.05 0.01	0.05 0.01	0.05 0.01	
Pennsylvania gasoline	30-30	30-25 30-28	26-20 27-22	30-28 30-28	
California gasoline	29-26	26-20 26-20	24-16 25-20	27-22 28-23	
Mid-Continent gasoline	30-28	20-22 29-22	25-19 26-21	30-25 30-26	

In the above table the first figure to the left of the dash in each case indicates the color of the gasoline plus inhibitor before exposure to a standardized arc light test which is roughly equivalent to two hours exposure to full June sunlight. An analysis of the data shows that both the color and color stability of the three gasolines was worse when using the aged tar fraction than when using the fresh tar fraction and that the fraction restored by treatment according to the present process was somewhat better than the original fresh tar fraction, thus indicating definitely the value of the invention from a commercial standpoint.

55 Substantially the same results are obtainable when treating the above mentioned fraction in vapor phase if the zinc chloride solution is atomized into the vapors as they enter a settling chamber.

60 The nature of the invention is sufficiently described in the specification and the results obtainable by its use are exemplified by the numerical data used but the invention is broad in scope and is not to be unduly limited by the descriptive material and examples.

I claim as my invention:

1. A process for the treatment of wood tar to

improve its inhibiting properties in respect to preventing deterioration of motor fuels which comprises, subjecting the said wood tar to a polymerizing treatment in the presence of a polymerizing salt of a metal.

2. A process for the treatment of wood tar to improve its inhibiting properties in respect to preventing deterioration of motor fuels which comprises, subjecting the said wood tar to a polymerizing treatment in the presence of a polymerizing metallic halide.

3. A process for the treatment of a tar derived from hardwood to improve its inhibiting properties in respect to preventing deterioration of motor fuels which comprises, subjecting the said tar to a polymerizing treatment in the presence of a polymerizing metallic halide.

4. A process for the treatment of a fraction derived from wood tar to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said fraction derived from wood tar to a polymerizing treatment in the presence of a polymerizing chloride of a metal.

5. A process for the treatment of a fraction derived from hardwood tar to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said fraction derived from hardwood tar to a polymerizing treatment in the presence of a polymerizing chloride of a metal.

6. A process for the treatment of a distillate derived from wood tar to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said distillate derived from wood tar to a polymerizing treatment in the presence of a polymerizing chloride of a metal.

7. A process for the treatment of a distillate derived from wood tar boiling substantially below 425° F. to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said distillate derived from wood tar boiling substantially below 425° F. to a polymerizing treatment in the presence of a polymerizing chloride of a metal.

8. A process for the treatment of a fraction derived from wood tar to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said fraction derived from wood tar to a polymerizing treatment in the presence of zinc chloride.

9. A process for the treatment of a distillate derived from wood tar boiling substantially below 425° F. to improve its qualities as an inhibitor in preventing the deterioration of cracked gasoline in respect to the formation of gum which comprises, subjecting the said distillate derived from wood tar boiling substantially below 425° F. to a polymerizing treatment in the presence of aluminum chloride.

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