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PREPARATION OF CHROMIUM ALKYL SALICYLATE ANTI-STATIC AGENTS

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This invention is concerned with means for preventing the buildup of electrostatic charges in hydrocarbon fuel. More specifically, the invention relates to novel methods for the preparation of particular anti-static additives for fuels as well as to the use thereof.

Liquid hydrocarbons and hydrocarbon mixtures, such as petroleum fractions, have a very low electrical conductivity. As a result the liquid may become electrically charged when it moves relative to a surface or interface. Movement relative to a surface occurs, for example, when the liquid is pumped through a hose or when it is used for cleaning textile materials. Movement relative to an interface occurs, for example, when suspended drops of water settle from the liquid hydrocarbons. The electrostatic charges may cause sparks and thus cause ignition or explosion of mixtures of air and hydrocarbons.

This danger arises particularly when the air in contact with the hydrocarbon contains between approximately 1 and 7% by volume of hydrocarbon vapor. Thus, at room temperature (approximately 20° C.) heavy gasolines and light kerosenes are extremely dangerous. At lower temperatures the danger becomes greater with lighter fractions, such as light gasolines, and at higher temperatures the danger becomes greater with heavier fractions, such as heavy kerosenes.

Electrostatic charging occurs to a particularly high degree when hydrocarbons are pumped at high speeds. Heavy gasolines and kerosenes are often used as fuels for turboprop and jet aircraft. When fueling aircraft, the fuels are generally pumped through relatively narrow hoses, which makes it necessary to pump them at high speeds. Pumping through filters as is frequently done when fueling aircraft, may give rise to high electrostatic charges. It will be clear that in this case there is a considerable explosion hazard. However, some danger still exists when hydrocarbons are pumped at lower speeds, as is the case when storage tanks are filled in refineries, and this hazard is greatly increased in the presence of water.

The formation of electric charges in hydrocarbons and other organic liquids having a dielectric constant of 8 or less can be prevented by increasing their electrical conductivity by the addition of a chromium salt of an alkyl salicylic acid containing at least one alkyl substituent having eight or more carbon atoms. The chromium salt may be used with or without other compounds which will increase the electrical conductivity of organic liquids after being added thereto. These compounds may, for example, be of the type which, together with the chromium salt, increase the electrical conductivity of organic liquids to a value which is at least five times the sum of the electrical conductivities obtained when each of the two additives is employed separately. In this respect salts of dioctyl sulphosuccinic acid, in particular the calcium salt, are especially suitable.

Chromium alkyl salicylates may be prepared from the

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corresponding alkali metal salts. For example, a mixture of sodium or potassium salts of alkyl salicylic acids containing at least one alkyl substituent having 14-18 carbon atoms is converted with a 10% excess of a 15% solution of chromium nitrate in ethanol at a temperature of 75° C. into the corresponding chromium salts, after which the alcohol is distilled off at a bottom temperature of not more than 100° C., 30% by volume of benzene is added and any alcohol still present in the mixture as well as water (for example water of crystallization of the chromium nitrate) is removed by azeotropic distillation. In this process, therefore, the temperature is increased after the conversion of the alkali metal salicylates with chromium salts, this being necessary for removing the solvent present in the mixture formed.

During the execution of the known process described above, there might be a risk of explosion owing to the formation of alkali metal nitrates. This drawback could be obviated by the use of an inorganic chromium salt other than chromium nitrate. Experiments have shown, however, that by using such a salt a product is obtained which can increase the electrical conductivity of organic liquids to a lesser extent than the product prepared from an alkali metal salt and chromium nitrate. It has been found that the effect of the conversion product on the electrical conductivity of organic liquids is increased by subjecting the product to a certain after-treatment.

It is an object of the present invention to provide improved anti-static hydrocarbon fuel compositions. It is another object of the invention to provide an improved process for the preparation of anti-static additives. It is a particular object of the invention to provide an improved process for the preparation of such additives having enhanced performance properties and reduced preparation hazards. Other objects will become apparent during the detailed description of the invention.

Now in accordance with the invention, the chromium salt of an alkyl salicylic acid containing at least one alkyl substituent having 8 or more carbon atoms is obtained by reacting a corresponding alkali metal salt with at least a stoichiometric amount of a halide of trivalent chromium and exposing the resultant reaction product in the presence of oxidizing agents of the groups consisting of nitrated hydrocarbons, inorganic nitrates and peroxides to a temperature of 100° C.-200° C. for 1-4 hours.

Alkali metal salts of alkyl salicylic acids may be prepared on a large scale, for example, by alkylation of phenol followed by conversion of the alkyl phenols into alkali metal phenates and carboxylation of these phenates by the Kolbe method. Phenol may be alkylated with 1-4 C₈₋₂₂ alkyl radicals. One method comprises alkylation with a mixture of olefins containing from 14-18 carbon atoms and obtained by cracking paraffin wax, whereby a mixture of mono- and di-C₁₄₋ to C₁₈-alkyl phenols is formed. The alkylation is carried out in the presence of a catalyst, for example zinc chloride and hydrochloric acid. Suitable alkyl radicals comprise octyl, nonyl, decyl, dodecyl, tetradecyl, octadecyl, including both straight chains and branched isomers thereof.

The alkyl phenols are then converted into the corresponding alkali metal phenates, for example sodium alkyl phenates. A suitable method of carrying out this conversion comprises heating the phenol with an alkali metal hydroxide in a lower alcohol medium, adding a higher boiling solvent for the phenate and distilling off the alcohol.

The alkali metal alkyl phenates are carboxylated with CO_2 by the Kolbe method. The carboxylation may be carried out without solvent but is preferably effected in the presence of an inert solvent such as xylene. Suitable carboxylation methods are described, for instance, in the British patent specifications 734,598, 734,622, and 738,359.

The carboxylation reaction does not proceed to completion and the reaction product (carboxylate) contains unconverted alkyl phenate. In addition, the carboxylate may contain other by-products such as alkyl phenols and alkali metal salts of di-carboxylic acids derived from the alkyl phenates by introducing two carboxylate groups.

The alkyl phenates and the alkyl phenols may be removed from the carboxylate. For example, the carboxylate is acidified and then neutralized with an alkali metal hydroxide, the alkyl salicylic acids being converted into the alkali metal salts and the alkyl phenols remaining unconverted; the alkyl phenols may be extracted by means of a liquid aliphatic hydrocarbon, such as pentane, from a solution of a mixture of alkali metal salts of alkyl salicylic acids and alkyl phenols in a mixture of water and alcohol (for example a mixture of equal parts of water and isopropanol).

The resultant alkali metal salts may be used as starting materials for the preparation according to the invention of chromium salts of alkyl salicylic acids containing at least one alkyl substituent with eight or more carbon atoms. It is, however, also possible to omit the removal of the alkyl phenates and the alkyl phenols from the carboxylate and to use this reaction product obtained by carboxylation of the alkali metal alkyl phenates with CO_2 by the Kolbe method as starting material in the process according to the invention.

For the preparation according to the reaction a solution of alkali metal alkyl salicylates, for example in a hydrocarbon or an alcohol, is preferably used. The alkali metal alkyl salicylate may be converted by heating at 35–90° C. for 0.1–4 hours with a bromide of trivalent chromium, but the use of chromium trichloride, for example dissolved in an alcohol such as methanol, is preferred, utilizing 1–1.15 equivalents of chromium halide per equivalent of salicylate.

The chromium alkyl salicylate may, for example, be heated in the presence of one or more nitro-hydrocarbons, such as nitro-methane, nitro-benzene, nitro-toluene and nitro-naphthalene and their analogs and homologues having 1–4 nitro groups per molecule and 0–4 alkyl substituents of 1–4 carbon atoms each. Of these nitro-compounds the aromatic ones are to be preferred. Synergistic results are obtained by using 1–5% by weight of hydrogen peroxide, based on the salicylate, in conjunction with the nitro-hydrocarbon. Nitro-alkanes or nitrated aromatics may be utilized. Nitro-alkanes particularly preferred include C_{1-4} nitro-alkanes containing 1–4 nitro groups per molecule including nitro-methane, nitro-ethane, nitro-propane and nitro-butane. Nitrated aromatics include mono and dicyclic hydrocarbons having 6–20 carbon atoms per molecule. The compounds mentioned may be used separately, but the after-treatment of the chromium alkyl salicylate formed may also be carried out in the presence of more than one oxidizing agent. The effect of the chromium alkyl salicylate is considerably increased, for example by using hydrogen peroxide together with nitro-benzene.

The oxidizing agents need only be employed in small quantities preferably 1–15%. Thus, for example, a quantity of less than 5% by weight of nitro-hydrocarbons such as nitro-methane, nitro-benzene and nitro-naphthalene is sufficient to obtain a good result. Suitable inorganic nitrates include ammonium nitrate, and chromium nitrate, while effective peroxides include hydrogen peroxide, acyl peroxides such as benzoyl peroxide and alkyl peroxides such as di-tert-butyl peroxide.

It is preferred to expose the chromium alkyl salicylate to a temperature not exceeding 200° C. The lower the temperature to which the reaction product is exposed, the longer is the heating time required to obtain the desired effect. When a temperature of 150° C. or lower, for example 120° C., is employed, the chromium alkyl salicylate is preferably exposed to that temperature for at least 1 hour. If the chromium alkyl salicylate is subjected to a temperature of 150° C. or higher, the heating period is preferably at least a quarter of an hour.

After a mixture of chromium alkyl salicylates having about one alkyl substituent with 14–18 carbon atoms and sodium chlorides has been obtained from a solution of chromium trichloride in methanol and a solution of carboxylate and xylene, an oxidizing agent can be added, after which the temperature is raised to 120° C., for example. During this heating, the methanol is first removed by azeotropic distillation and then the water. The mixture is subsequently heated to 120° C. for two hours, after cooling to approximately 70° C., and deposit is removed by filtration.

However, the sodium chloride may also be removed by water-washing after the reaction of chromium trichloride with sodium carboxylate before the reaction product is heated in the presence of an oxidizing agent.

The invention will be illustrated with reference to the following example.

Example

Phenol is alkylated in the presence of zinc chloride and hydrochloric acid with a mixture of olefins containing 14–18 carbon atoms and obtained by cracking a paraffin wax. The alkyl phenol is dissolved in xylene and converted into the corresponding sodium alkyl phenates by heating it together with a 45% by weight aqueous solution of sodium hydroxide. The water is removed by azeotropic distillation. The phenate dissolved in xylene is carboxylated with CO_2 at super-atmospheric pressure. In addition to xylene the carboxylate contains unconverted sodium alkyl phenates.

35% by weight of additional xylene is added to the resultant solution of sodium carboxylate in xylene. Chromium trichloride is added, with stirring, to part of this solution in an amount of 100% equivalents based on the amount of sodium present in the carboxylate as a 12% by weight solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in methanol containing 5% by weight of water. To another part of the solution of sodium carboxylate, chromium trichloride is added in an amount of 105% equivalents based on the amount of sodium present in the carboxylate in the same form as described above. The two mixtures are refluxed to 70° C. while being stirred. The temperature is then increased to 120° C. and the methanol and the water are azeotropically distilled off. The resultant reaction mixtures are cooled to approximately 50° C. and filtered. The filtrates which contain 2% by weight of chromium are the final products containing chromium alkyl salicylates having about one alkyl substituent with from 14–18 carbon atoms and are hereinafter termed Cr-AC.

Each solution is divided into a number of parts, one of which is not subjected to an after-treatment, another heated to a certain temperature for a certain time without an additive, the others being exposed to such a heat treatment in the presence of an additive.

The resultant products in an amount of 0.0001% by weight, together with calcium dioctyl sulphosuccinate (termed Ca-AS hereinafter) in an amount of 0.0001% by weight are added to gasoline with a boiling range of 80–110° C. Of these solutions the conductivity is measured by the cell method described on page 87 of A. Klinkenberg and J. L. van der Minne, "Electrostatics in the Petroleum Industry," Elsevier Publishing Company (1958).

The results of these measurements are shown in the following table.

Preparation of Cr-AC Amount of CrCl ₃ with respect to Na present in carboxylate in percent equivalents	After-treatment			Conductivity in units of 10 ⁻¹⁴ Ohm ⁻¹ , cm. ⁻¹ of 80/110 gasoline with— 0.0001% by wt. Cr-AC +0.0001% by wt. Ca-AS
	Additive	Period in Hours	Temp., °C.	
100	No after-treatment			5,050
100	None	1	120	5,050
100	3% by weight of nitro-benzene	1	120	7,400
100	3% by weight of H ₂ O ₂ (30%)	0.25	150	7,450
100	3% by weight of H ₂ O ₂ (30%) + 3% by weight of nitro-benzene	0.25	150	10,100
100	7% equi. of Cr(NO ₃) ₃	1	120	7,200
105	No after-treatment			5,050
105	None	0.25	150	5,320
105	1% by weight of nitro-methane	0.25	150	6,500
105	2% by weight of nitro-naphthalene	0.25	150	8,100
105	1% by weight of nitro-benzene + 1% by weight of H ₂ O ₂ (30%)	0.25	150	8,100
105	1% by weight of nitro-benzene	0.25	150	7,000
105	1% by weight of H ₂ O ₂ (30%)	0.25	150	5,700
105	10% equi. of Cr(NO ₃) ₃	0.25	150	5,320

The chromium alkyl salicylate solutions are heated immediately after the addition of oxidizing agents mentioned in the table.

The following facts can be deduced from the table.

Heating Cr-AC without additive has no appreciable effect on the electrical conductivity of gasoline to which Cr-AC together with Ca-AS was added in the amounts given in the table, even though Cr-AC was prepared with the use of an excess of chromium trichloride. The effect of Cr-AC as a means for increasing the electrical conductivity of gasoline is markedly raised if the Cr-AC is heated to a temperature exceeding 100° C., in the presence of oxidizing agents such as the additives mentioned in the table.

The anti-static additives or mixtures thereof should be incorporated in a hydrocarbon liquid in a concentration of at least about 1×10⁻⁹, more especially at least 1×10⁻⁷ gram atoms of the metal per liter. The concentration of the chromium salt should not be greater than about 1×10⁻⁵ gram atoms of chromium per liter, and preferably not greater than 1×10⁻⁶ gram atoms of chromium per liter. The chromium salts may be utilized without any modifying anti-static additive but more preferably are combined with an auxiliary additive, preferably an alkaline earth metal salt of a dialkyl sulfo aliphatic dicarboxylic ester containing 4-10 carbon atoms in at least one of the alkyl groups, the ratio of gram atoms of the chromium in the chromium salts present then being from about 1:1 to about 10:1 gram atoms of the alkaline earth metal and said alkaline earth metal salt.

The alkaline earth metal salts are described in the United States Patent, U.S. 2,028,091 and preferably are the calcium salts, especially the calcium di-C₈+ alkyl sulfosuccinate, but such salts of the other alkaline earth metals, i.e., of magnesium, strontium, and barium are also advantageous in accordance with the invention.

The hydrocarbon liquids in which the combination additive of the invention are advantageously incorporated are preferably those which normally boil within the range of from about -40° F. to about 700° F., i.e., those which are generally referred to a hydrocarbon distillates. The invention is particularly applicable to petroleum distillates in the gasoline and kerosene boiling ranges, such as gasoline (both motor and aviation), aviation turbine fuel of the JP-1, JP-4, and JP-5 types, VM and P naphtha, cleaner's naphtha, lighter fluid, mineral spirits, rubber solvent, lacquer diluent, insecticide base, kerosene, and special boiling range hydrocarbon solvents of all kinds such as direct cuts of xylenes and non-aromatics boiling in or near the xylene range, or similar toluene and benzene cuts, and also extracts and raffinates (e.g., from

SO₂ or furfural extraction) obtained from such cuts. The invention is of greatest benefit and importance in the case of hydrocarbon distillates the vapors of which are likely to form explosive mixtures with air in atmospheric storage, i.e., mixture which contains from about 1% to about 8% by volume of hydrocarbon vapor. Those with Reid vapor pressures of from about 0.1 to about 5 p.s.i. at 100° F. are most likely to form such explosive mixtures in temperate climates.

We claim as our invention:

1. Process for the preparation of an anti-static agent for hydrocarbon fuels which comprises heating an alkali metal salt of a C₈₋₂₀ alkyl salicylic acid with 1-1.15 equivalents of a chromium trihalide per equivalent of said acid, whereby a chromium alkyl salicylate is formed, and exposing the salicylate to a temperature of 100-200° C. in the presence of 1.0-15% by weight of an oxidizing agent of the group consisting of (a) a nitrohydrocarbon selected from the group consisting of C₁₋₄ nitroalkanes containing 1-4 nitro groups and mono- to di-nitro-aromatic hydrocarbons having 6-20 carbon atoms per molecule, (b) an inorganic nitrate selected from the group consisting of ammonium and chromium nitrate and (c) a peroxide selected from the group consisting of hydrogen, acyl and alkyl peroxides, whereby an anti-static agent having increased conductivity characteristics is formed.

2. Process for the preparation of an anti-static agent for hydrocarbon fuels which comprises heating an alkali metal salt of a C₈₋₂₀ alkyl salicylic acid with 1-1.15 equivalents of a chromium trihalide per equivalent of said acid, whereby a chromium alkyl salicylate is formed, and exposing the salicylate to a temperature of 100-200° C. in the presence of 1.0-15% by weight chromium nitrate, whereby an anti-static agent having increased conductivity characteristics is formed.

3. Process for the preparation of an anti-static agent for hydrocarbon fuels which comprises heating an alkali metal salt of a C₈₋₂₀ alkyl salicylic acid with 1-1.15 equivalents of a chromium trihalide per equivalent of said acid, whereby a chromium alkyl salicylate is formed, and exposing the salicylate to a temperature of 100-200° C. in the presence of 1.0-15% by weight of a nitrohydrocarbon selected from the group consisting of C₁₋₄ nitroalkanes containing 1-4 nitro groups and mono- to di-nitro-aromatic hydrocarbons having 6-20 carbon atoms per molecule, whereby an anti-static agent having increased conductivity characteristics is formed.

4. A process according to claim 3 wherein the nitrohydrocarbon is supplemented with 1-5% by weight, based on the chromium alkyl salicylate of hydrogen peroxide.

5. Process for the preparation of an anti-static agent for hydrocarbon fuels which comprises heating an alkali metal salt of a C_{8-20} alkyl salicylic acid with 1-1.15 equivalents of a chromium trihalide per equivalent of said acid, whereby a chromium alkyl salicylate is formed, and exposing the salicylate to a temperature of 100-200° C. in the presence of 1.0-15% by weight ammonium nitrate, whereby an anti-static agent having increased conductivity characteristics is formed.

6. Process for the preparation of an anti-static agent for hydrocarbon fuels which comprises heating an alkali metal salt of a C_{8-20} alkyl salicylic acid with 1-1.15 equivalents of a chromium trihalide per equivalent of said acid, whereby a chromium alkyl salicylate is formed, and exposing the salicylate to a temperature of 100-200° C. in the presence of 1.0-15% by weight of a peroxide selected from the group consisting of hydrogen, acyl and alkyl peroxides, whereby an anti-static agent having increased conductivity characteristics is formed.

7. Process for the formation of an anti-static agent for hydrocarbon fuels which comprises heating sodium salts of $C_{(14-18)}$ mono alkyl salicylic acids with 1-1.05 equivalents of chromium trichloride per equivalent of

said acids, whereby the corresponding chromium salicylates are formed, and exposing the salicylates to a temperature of 120-150° C. for 0.25-1 hour in the presence of 1.5% by weight of a mono-nitro aromatic hydrocarbon having 6-10 carbon atoms per molecule whereby an anti-static agent having increased conductivity characteristics in hydrocarbons is formed.

8. A process according to claim 7 wherein the nitro-hydrocarbon is nitro-benzene.

9. A process according to claim 7 wherein the nitro-hydrocarbon is nitro-naphthalene.

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