

1

2,922,801

OIL-SOLUBLE CERIC SALTS AND METHOD
OF PREPARING THE SAME

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This invention relates to a novel class of oil-soluble ceric salts and to the process of preparing the same. More particularly, this invention relates to a group of novel oil-soluble ceric salts such as ceric alkyl sulfates, ceric alkyl mono aromatic sulfonates, ceric sulfonates of an aliphatic polycarboxylic acid dialkyl ester and ceric aliphatic hydrocarbon sulfonates and to the process of preparing the same.

One of the objects of the present invention is to produce a class of oil-soluble ceric salts which will have utility particularly as graft polymerization initiators in a vinyl polymerization system. These and other objects of the present invention will be discussed in greater detail hereinbelow.

This application is a continuation-in-part of our earlier application having the Serial No. 628,212, filed December 14, 1956, entitled "Process for Polymerization and the Products Produced Thereby." Said application is a continuation-in-part of our parent case having the Serial No. 577,641, filed April 12, 1956, entitled "Process for Polymerization and the Products Produced Thereby," now abandoned.

In producing the novel oil-soluble ceric salts of the present invention, one may react an inorganic ceric salt with an alkali metal salt of a material selected from the group consisting of an alkyl sulfate, an alkyl mono aromatic sulfonate, a sulfonate of an aliphatic polycarboxylic acid dialkyl ester and an aliphatic hydrocarbon sulfonate. The inorganic ceric salts may be any one of the following: ceric nitrate, ceric ammonium nitrate, ceric perchlorate and the like. These inorganic ceric salts may be used either singly or in combination with one another.

The alkali metal salts used as starting materials in the practice of the process of the present invention may be the sodium salts, potassium salts, lithium salts, and the like. Included in the group of alkali metal salts which may be used are sodium monobutyl acid sulfate, potassium monoamyl acid sulfate, sodium mono-octyl acid sulfate, sodium monolauryl acid sulfate, potassium monodecyl acid sulfate, lithium mono-undecyl acid sulfate, sodium octyl benzene sulfonate, potassium decyl benzene sulfonate, sodium dioctyl sulfosuccinate, lithium diheptyl sulfoglutarate, potassium didecyl sulfosuberate, sodium dilauryl sulfosubacate, potassium diamyl sulfomaleate, sodium dimethyl sulfofumarate, sodium dibutyl sulfodimethyl succinate, potassium dilauryl sulfomethyl glutarate, sodium butyl sulfonate, potassium hexyl sulfonate, lithium octyl sulfonate, potassium decyl sulfonate, sodium dodecyl sulfonate, and the like.

Among the oil-soluble ceric alkyl sulfates which may be prepared according to the process of the present invention are those ceric alkyl sulfates in which the alkyl group contains between 4 and 20 carbon atoms and preferably between 8 and 12 carbon atoms. Included in the group are ceric butyl sulfate, ceric amyl sulfate, ceric hexyl sulfate, ceric heptyl sulfate, ceric octyl sulfate, ceric nonyl sulfate, ceric decyl sulfate, ceric undecyl sulfate,

2

ceric dodecyl sulfate, ceric tridecyl sulfate, ceric tetradecyl sulfate, ceric pentadecyl sulfate, ceric hexadecyl sulfate, ceric heptadecyl sulfate, ceric octadecyl sulfate, ceric nonadecyl sulfate, and ceric eicosyl sulfate. The alkyl groups in these ceric alkyl sulfates may be either a straight chain or a branch chain.

Among the oil-soluble ceric alkyl mono aromatic sulfonates which may be prepared according to the present invention are those in which the alkyl groups attached to the mono aromatic ring contain between 3 and 20 carbon atoms, and preferably between 8 and 12 carbon atoms. The mono aromatic grouping in said sulfonates may be phenyl, naphthyl, anthracyl, triphenyl, perylyl, and the like. More specifically, these compounds include ceric butyl benzene sulfonate, ceric hexyl benzene sulfonate, ceric octyl benzene sulfonate, ceric nonyl benzene sulfonate, ceric decyl benzene sulfonate, ceric dodecyl benzene sulfonate, ceric octadecyl benzene sulfonate, ceric isopropyl naphthalene sulfonate, ceric heptyl naphthalene sulfonate, ceric tetradecyl naphthalene sulfonate, ceric heptadecyl naphthalene sulfonate, ceric eicosyl naphthalene sulfonate, and the like.

Among the oil-soluble ceric sulfonates of an aliphatic polycarboxylic acid dialkyl ester which may be prepared from the process of the present invention are those prepared from the sodium salts of a sulfonate of an aliphatic polycarboxylic acid dialkyl ester. These sodium salts and other alkali metal salts are shown in considerable detail in the U.S. Patent 2,028,091. The aliphatic dicarboxylic acids which may be used as starting materials include malonic, succinic, glutaric, sebacic, adipic, pimelic, suberic, azelaic, citric, tartaric, malic, maleic, fumaric, aconitic, itaconic, and the like. The diesters of these acids are prepared by reacting an aliphatic monohydric alcohol containing from 1 to 15 carbon atoms and preferably containing from 4 to 8 carbon atoms so as to form the dialkyl ester of said polycarboxylic acid. More specifically the following oil-soluble ceric salts may be prepared by the process of the present invention: ceric dihexyl sulfosuccinate, ceric dioctyl sulfosuccinate, ceric diheptyl sulfoglutarate, ceric didecyl sulfosuberate, ceric dilauryl sulfosubacate, ceric diamyl sulfomaleate, ceric dimethyl sulfofumarate, ceric dibutyl sulfodimethyl succinate, ceric dilauryl sulfomethyl glutarate, ceric dipentadecyl sulfosuccinate, and the like.

Among the oil-soluble ceric aliphatic hydrocarbon sulfonates which may be prepared in keeping with the process of the present invention are those in which the aliphatic hydrocarbon contains between 4 and 20 carbon atoms and preferably those containing between 8 and 12 carbon atoms. More specifically, the oil-soluble ceric aliphatic hydrocarbon sulfonates of the present invention include ceric butyl sulfonate, ceric amyl sulfonate, ceric hexyl sulfonate, ceric octyl sulfonate, ceric decyl sulfonate, ceric dodecyl sulfonate, ceric tetradecyl sulfonate, ceric hexadecyl sulfonate, ceric octadecyl sulfonate, ceric eicosyl sulfonate, and the like.

In the practice of the process of the present invention, the inorganic ceric salt is introduced into the reaction sphere with an alkali metal salt of an alkyl sulfate or an alkyl mono aromatic sulfonate or a sulfonate of an aliphatic polycarboxylic acid dialkyl ester or an aliphatic hydrocarbon sulfonate in an aqueous medium. The temperature of the reaction may be controlled between about 0° C. and 40° C. and preferably between 20 and 25° C. The pH of the system should be adjusted to 3.5 or below and preferably between about 1 and 2. The system will be rendered acidic by the use of an acid material and preferably an inorganic acid material such as nitric acid, perchloric acid, and the like. In order to insure substantially complete reaction between the inorganic ceric salt and the alkali metal salts of the alkyl sulfates or the alkyl

mono aromatic sulfonates or the sulfonates of an aliphatic polycarboxylic acid dialkyl ester or the aliphatic hydrocarbon sulfonates, agitation is preferred as contrasted with quiescence in the course of reaction. For satisfactory yields, one should use at least 1 mol of the alkali metal sulfate or sulfonate per mol of the ceric inorganic salt and as much as 4 mols of the alkali metal sulfate or sulfonate per mol of the ceric inorganic salt. Larger quantities of the alkali metal sulfate or sulfonate may be used such as 5 mols or even 6 but no appreciable advantage is to be gained. It is preferred that the mol ratio of the alkali metal sulfates or sulfonates per mol of ceric inorganic salt be controlled between about 1.5:1 and 2:1, respectively.

The novel oil-soluble ceric salts of the present invention will find utility in the polymerization of polymerizable monomeric compounds such as styrene, acrylonitrile, vinyl acetate, acrylamide, and the like, and particularly in a system in which a grafting mechanism is being carried out with a polymeric organic reducing agent such as when an aqueous emulsion system is utilized.

In order that the concept of the present invention may be more completely understood, the following examples are set forth in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation on the case except as is indicated in the appended claims.

Example 1

Into a suitable reaction vessel equipped with a mechanical stirrer, there is introduced a solution of 11 parts of ceric ammonium nitrate in 100 parts of water at room temperature. With constant stirring, there is added thereto a solution of 15.4 parts of sodium dihexyl sulfosuccinate in 100 parts of water. The stirring is continued even after the addition is completed and is stopped only when all of the precipitate has come out of the blended solutions. The precipitate is separated from the water by a simple filtration producing a yield of 14 parts of ceric dihexyl sulfosuccinate.

Example 2

A solution of 14.4 parts of sodium diamyl sulfosuccinate in 100 parts of water is added to a rapidly stirred solution of 11 parts of ceric ammonium nitrate in 100 parts of a 0.1 molar solution of nitric acid at 15° C. The resulting yellow precipitate, after separation by filtration and drying in vacuo at 45° C., weighed 12.6 parts and was identified as ceric diamyl sulfosuccinate.

Example 3

11 parts of ceric ammonium nitrate are dissolved in 100 parts of a 0.1 molar solution of nitric acid at 25° C. To this solution there is added, with rapid stirring, a solution of 13.8 parts of sodium dodecyl benzene sulfonate in 100 parts of water. The yellow precipitate which formed was separated by filtration and dried in vacuo at 45° C. The yield was 4.8 parts and was identified as ceric dodecyl benzene sulfonate. The ceric salt thus produced was soluble in ethyl acetate, benzene and chloroform.

Example 4

12 parts of sodium dodecyl sulfate was dissolved in 100 parts of water and the solution thus produced was added with rapid stirring to a solution of 11 parts of ceric ammonium nitrate in 100 parts of a 0.1 molar solution of nitric acid at 20° C. The resulting yellow precipitate was separated by filtration and dried in vacuo at 45° C. The resulting material was identified as ceric dodecyl sulfate and was soluble in benzene, methyl acrylate, methylene chloride, and methyl ethyl ketone.

Example 5

11 parts of ceric ammonium nitrate are dissolved in 100 parts of 0.1 N nitric acid at 20° C. To this is added with rapid stirring a solution of 8.7 parts of sodium octane sulfonate in 100 parts of water. The yellow precipitate is separated by filtration, washed with water, then dried in vacuo at 40-45° C. The yield is 5.7 parts.

The term oil soluble is one frequently used in the art and signifies solubility in an organic solvent, which solvent is itself not miscible with water. A plurality of these solvents have been recited hereinabove and a substantial plurality of said solvents are well known in the art. Further delineation is deemed to be unnecessary.

We claim:

1. An oil-soluble ceric salt selected from the group consisting of (1) a ceric alkyl sulfate, (2) a ceric alkyl arene sulfonate, (3) a ceric sulfonate of an unsubstituted aliphatic polycarboxylic acid dialkyl ester and (4) a ceric aliphatic hydrocarbon sulfonate.

2. An oil-soluble ceric alkyl sulfate.

3. An oil-soluble ceric alkyl arene sulfonate.

4. An oil-soluble ceric sulfonate of an unsubstituted aliphatic polycarboxylic acid dialkyl ester.

5. An oil-soluble ceric aliphatic hydrocarbon sulfonate.

6. Ceric dihexyl sulfosuccinate.

7. Ceric diamyl sulfosuccinate.

8. Ceric dodecyl benzene sulfonate.

9. Ceric dodecyl sulfate.

10. Ceric dodecyl sulfonate.

11. A method for preparing an oil-soluble ceric salt which comprises reacting an inorganic ceric salt selected from the group consisting of ceric nitrate, ceric ammonium nitrate and ceric perchlorate with an alkali metal salt of a material selected from the group consisting of (1) an alkyl sulfate, (2) an alkyl arene sulfonate, (3) a sulfonate of an unsubstituted aliphatic polycarboxylic acid dialkyl ester and (4) an aliphatic hydrocarbon sulfonate.

12. A method for preparing an oil-soluble ceric salt comprising reacting an inorganic ceric salt selected from the group consisting of ceric nitrate, ceric ammonium nitrate and ceric perchlorate with an alkali metal salt of an alkyl sulfate.

13. A method for preparing an oil-soluble ceric salt comprising reacting an inorganic ceric salt selected from the group consisting of ceric nitrate, ceric ammonium nitrate and ceric perchlorate with an alkali metal salt of an alkyl arene sulfonate.

14. A method for preparing an oil-soluble ceric salt comprising reacting an inorganic ceric salt selected from the group consisting of ceric nitrate, ceric ammonium nitrate and ceric perchlorate with an alkali metal salt of a sulfonate of an unsubstituted aliphatic polycarboxylic acid dialkyl ester.

15. A method for preparing an oil-soluble ceric salt comprising reacting an inorganic ceric salt selected from the group consisting of ceric nitrate, ceric ammonium nitrate and ceric perchlorate with an alkali metal salt of an aliphatic hydrocarbon sulfonate.

16. A method comprising reacting ceric ammonium nitrate with sodium dihexyl sulfosuccinate.

17. A process comprising reacting ceric ammonium nitrate with sodium diamyl sulfosuccinate.

18. A process comprising reacting ceric ammonium nitrate with sodium dodecyl benzene sulfonate.

19. A process comprising reacting ceric ammonium nitrate with sodium dodecyl sulfate.

20. A process comprising reacting ceric ammonium nitrate with sodium dodecyl sulfonate.

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