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PROCESS FOR MAKING OIL-SOLUBLE CHROMIUM CARBOXYLATES

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This invention relates to a novel and economic process for manufacturing trivalent chromium salts of olefinically unsaturated long chain fatty acids, which salts have low solubility in water and high solubility in liquid hydrocarbons and are particularly useful as addition agents for petroleum hydrocarbon products.

Trivalent chromium salts of organic acids have been prepared by metathetical reactions of the acid or a salt thereof with a suitable compound of trivalent chromium. However, since chromium is normally recovered from nature in its hexavalent state, it is desirable for reasons of economy to be able to employ hexavalent chromium directly in the preparation of trivalent chromium compounds. Stover, in U.S. Patent 2,615,031, discloses the formation of trivalent chromium salts of acetic acid and other low molecular weight monobasic acids having not over 6 carbon atoms by reducing hexavalent chromium to trivalent chromium with glycollic acid in the presence of the carboxylic acid. The trivalent chromium carboxylate is obtained as an aqueous solution containing other products of reaction. However, it should be noted that, in aqueous media, a water-soluble trivalent chromium carboxylate, such as Cr(III) acetate, is not a simple salt product, but exists as complex hydrated species which are more or less extensively hydrolyzed. Udy, "Chromium," vol. 1, pages 229-233, Am. Chem. Soc. Monograph, Reinhold Publ. Corp., 1956.

Hervey, in U.S. Patent 2,178,874, employs ethylenically unsaturated fatty acids to reduce sodium dichromate in sulfuric acid, whereby ethylenic bonds of the acids are oxidatively cleaved, with the resultant formation of saturated carboxylic acids of lower carbon content, e.g. pelargonic and azelaic acids from oleic acid. The organic products, comprising the newly formed carboxylic acids, form a supernatant layer from which the reduced aqueous chromium sulfate solution may be readily separated. According to Hervey, the organic acid layer may contain small amounts of reduced chromium compounds which are easily extracted out by washing with aqueous sulfuric acid.

An object of this invention is to provide a new and economic process, involving in situ formation of trivalent chromium from hexavalent chromium, for the production of oil-soluble trivalent chromium salts of water-insoluble ethylenically unsaturated fatty acids. A particular object is to provide such a process whereby unhydrolyzed, substantially pure oil-soluble trivalent chromium unsaturated fatty carboxylates, or solutions thereof in organic solvents, are obtained substantially without oxidative degradation of the ethylenic bonds. A further object is to advance the art. Still other objects will become apparent from the following disclosure.

The foregoing and other objects are accomplished by the process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises

(A) Reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of

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- (a) At least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) A reducing agent for said dichromate in an amount sufficient to completely reduce the chromium to Cr(III), said reducing agent having a standard oxidation potential in the range of minus 0.25 to plus 0.5 volt;
- (c) From about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;

(B) Maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and

(C) Separating the resultant Cr(III) carboxylate product from the by-product aqueous phase.

By the above defined process, employing in combination the materials, proportions and conditions set forth, the oil-soluble trivalent chromium salts of unsaturated long chain fatty acids are obtained simply, directly, and cheaply in high yields from low cost sources of chromium. It has been found that the recited reducing agents are more readily oxidized than the unsaturated acid, whereby the unsaturated acid does not become oxidized and, due to the controlled amounts of acid employed, the chromium salt of the desired acid is obtained in a high degree of purity.

As disclosed in British Patent 749,898, of June 6, 1956, and by Van der Minne et al. in U.S. Patent 3,012,969, it is highly desirable to add to liquid hydrocarbons, particularly distillate fuel oils and the like, substances or combinations of substances which increase the electrical conductivity of the hydrocarbons and thereby lessen the hazards of static-induced explosions and/or fires occurring during handling of such fuel oils by the dissipation of electrical charges as they are generated. Various metal salts of organic acids are known to be useful for such purposes, particularly when employed with lecithin and like materials. There are very few chromium salts of organic acids which are commonly available and they are generally quite expensive and of insufficient purity for use for such purposes. The chromium(III) carboxylates, produced by the process of the present invention, are particularly effective to improve the electrical conductivity of distillate hydrocarbon fuels, such as fuel oils and JP-5 jet fuel, particularly when employed in conjunction with lecithin and like materials. Also, due to the advantages of the process of this invention, the chromium carboxylates so produced are sufficiently inexpensive and sufficiently pure to render them particularly desirable for such use.

The unsaturated fatty acids that may be used in the process of this invention for conversion into trivalent chromium carboxylates having low solubility in water and high solubility in liquid hydrocarbon media are those normally containing from about 10 to 22 carbons, more usually 12 to 18 and, in particular, the abundantly available 18 carbon species, exemplified by oleic and linoleic acids, including naturally occurring mixtures containing them such as the tall oil acids. Other ethylenically unsaturated acids that may be used are 9-decenoic, 10-undecenoic, 4-dodecenoic, 5-dodecenoic, palmitoleic, elaidic, petroselinic, linolenic, eleostearic, eicosenoic, erucic and cetoleic acids. It should be understood that such acids, obtained from natural sources, may contain minor proportions of saturated analogs. The term fatty acid composition which consists essentially of at least one ethylenically unsaturated fatty acid as used herein is meant to include a single pure unsaturated acid, a mixture of two or more of such acids,

and a mixture consisting essentially of as low as about 90 mole percent of one or more of the unsaturated acids and as high as about 10 mole percent of the saturated acids. The above acids have low solubility in water and form trivalent chromium salts having pronounced solubility in liquid hydrocarbons such as benzene, toluene, xylene, kerosene, jet fuel, diesel oil and burner oil.

Dichromates of sodium, lithium, potassium, rubidium, cesium, magnesium, calcium, strontium, and mixtures of any two or more thereof may be used. Alkali metal salts are preferred, particularly sodium dichromate for its low cost. Calcium dichromate is particularly useful when it is desired to produce an oil-soluble trivalent chromium unsaturated fatty carboxylate composition containing small amounts of calcium as more fully described hereinafter. The dichromate may be produced in situ from the corresponding chromate or from chromium trioxide, according to well known chemistry based on the fact that the trioxide is the anhydride of chromic and dichromic acid, H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$, and that the chromate and dichromate forms are interconvertible according to the reaction, $2\text{CrO}_4^{2-} + 2\text{H}^+ = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$.

According to the process of the invention, chromium in the hexavalent state Cr(VI) is reduced to the trivalent state Cr(III), while in the presence of an unsaturated acid, as defined above, which forms a water-insoluble, oil-soluble Cr(III) salt, by means of a reducing agent which is more easily oxidized than the unsaturated acid itself under the conditions of the process. The reduction normally is effected with a reducing agent for dichromate having a standard oxidation potential, relative to the hydrogen-hydrogen ion potential taken as zero, which falls in the range -0.25 to 0.5 volt, as illustrated below. A wide variety of reducing agents having the proper potential are known, including aliphatic mono- and polyhydric alcohols; hydroxyaldehydes; aldehydes; reducing acids such as formic acid, oxalic acid and in general aliphatic aldehyde and hydroxy carboxylic acids; and sulfurous substances such as sulfur dioxide, sulfurous acid and alkali and alkaline earth metal salts thereof. The term oxidation potential is used herein in the sense described by Latimer, in "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, 1952.

Reductants, representative of the indicated classes, and their relation to the dichromate system are tabulated and discussed below:

TABLE

	Reductant	Oxidant	E° , volts (25° C.)
A-----	$\text{H}_2\text{C}_2\text{O}_4$	$= 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	0.49
B-----	HCO_2H	$= \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	0.14
C-----	CH_3OH	$= \text{HCHO} + 2\text{H}^+ + 2\text{e}^-$	-0.19
D-----	$\text{HCHO} + \text{H}_2\text{O}$	$= \text{HCO}_2\text{H} + 2\text{H}^+ + 2\text{e}^-$	-0.06
E-----	$\text{C}_2\text{H}_5\text{OH}$	$= \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-$	-0.19
F-----	$\text{CH}_3\text{CHO} + \text{H}_2\text{O}$	$= \text{CH}_3\text{CO}_2\text{H} + 2\text{H}^+ + 2\text{e}^-$	0.12
G-----	$\text{CH}_3\text{CHO} + \text{HCO}_2\text{H}$	$= \text{CH}_3\text{COCO}_2\text{H} + 2\text{H}^+ + 2\text{e}^-$	-0.20
H-----	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	$= \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$	-0.20
I-----	$2\text{Cr}^{+++} + 7\text{H}_2\text{O}$	$= \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^-$	-1.33

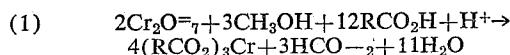
According to these data, the oxidized form (right-hand side) of the Cr(III)-Cr(VI) couple has sufficient energy to oxidize the reduced form (left-hand side) of any couple of higher positive potential (the more positive E° the stronger the reducing agent). That reduction of dichromate as in item I is actually effected in reasonable rates by each of the indicated reductants of higher potential, is amply illustrated in the literature in a variety of situations. It is believed that all such reductants (and the classes they represent) are operable for the present purpose and that none would interfere therewith. Note, from C, D and B of the table, that one mole of CH_3OH is capable of providing the 6 electrons needed to reduce one mole of dichromate, leading in the overall process to CO_2 and H_2O via formaldehyde and formic acid, both known to reduce dichromate. However, in the present process, it is arbitrarily assumed that methanol goes only

to formate [summarized by Equation 1 below] to assure complete utilization of dichromate. In other words, in terms of the quantity used, methanol is herein classed with the higher primary alcohols, which oxidize as far as the carboxylic stage (E and F above). This requires 1.5 moles of alcohol (to supply 6 electrons) per mole of dichromate.

Such substances as SO_4^{2-} (from oxidation of SO_2), formate complexes, oxalate complexes, and oxidation products of ethanol should not result in objectionable contamination in the oil-soluble Cr(III) carboxylates of this process and, if they should form, they can be largely removed by washing the product with water or aqueous media as described hereinafter.

The aliphatic monohydric and polyhydric alcohols, including the saturated and the ethylenically unsaturated alcohols, normally are the acyclic primary alcohols of 1 to 22 carbon atoms which consist of the elements carbon, hydrogen and oxygen. By "primary alcohol" is meant that at least one hydroxyl group is a primary alcohol group. The primary monohydric alcohols, especially the water-soluble members, constitute a preferred class which may be represented by the formula RCH_2OH where $\text{R}=\text{H}$, alkyl or alkenyl. Examples are methanol, ethanol, propanol, butanol, hexanol, isooctyl alcohol, oxo-octyl alcohol, decanol, oxo-tridecanol, lauryl alcohol, oleyl alcohol, 2-hexyldecanol, and the normal saturated and unsaturated aliphatic alcohols having from 8 to 22 carbon atoms which are manufactured from coconut kernel oils and sperm oil and are known to the art as "Lorol 5" alcohol and "Ocenol," respectively. When the unsaturated alcohols are employed in this process, oxidation takes place preferentially at the alcohol function.

As reducing agents, the primary alcohols provide the beneficial auxiliary effect of forming carboxylate anions in the reaction mass on being oxidized by said hexavalent chromium, which carboxylate anions help maintain the desired pH characteristics by buffer action. In one aspect of this invention, it is preferred to employ low molecular weight primary alcohols which form water-soluble alkali metal carboxylates having little or no emulsifying properties in water, that is, alcohols having less than 8 carbons, particularly methanol in a proportion of 1.5 to about 3 moles for each mole of dichromate. The stoichiometry of this process is represented by Equation 1 below showing the preferred combination of sodium dichromate and methanol:



R standing for an unsaturated hydrocarbon radical of an unsaturated fatty acid as defined.

The reducing agent is generally in excess, say 10-100%, preferably 20-50% molar excess, to ensure substantially complete reduction of Cr(VI) to Cr(III).

Those skilled in the art will recognize that, as indicated in the preceding table, dichromate can oxidize alcohols to carboxylic acids via intermediate aldehydes and that such aldehydes may be employed in place of the corresponding primary alcohols above in accordance with the stoichiometry of the tabulated reactions. There may also be used polyhydric alcohols, hydroxyaldehydes, aldehydocarboxylic acids and hydroxycarboxylic acids. Representative of such substances are ethylene glycol, glycerol, glucose, glyoxal, formaldehyde, acetaldehyde, butyraldehyde, octaldehyde, glyceric acid, glyoxalic acid, glycolic acid and lactic acid. Sulfurous acid may be employed as such, as its anhydride, SO_2 , or as an alkali metal or alkaline earth metal sulfite or bisulfite.

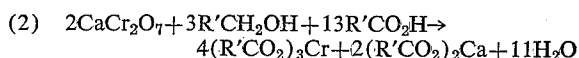
The total acid employed corresponds to 3-4 equivalents of hydrogen ion per chromium atom introduced as dichromate, at least 3 of said hydrogens being in the form of the carboxylic acid to be converted to Cr(III) carboxylate and from 0 to 1 equivalent as an acid having a

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dissociation constant (as measured in water) which is greater than 1×10^{-6} . The nature of this latter acid is believed not critical. Thus, the acidity represented by H^+ above in Equation 1 may be provided wholly in the form of said ethylenically unsaturated acid or in minor part by another carboxylic acid, preferably a water-soluble acid, such as formic acid or an acetic acid, or by a mineral acid such as hydrochloric acid, sulfuric acid or phosphoric acid. Preferably, the total acidity will be due to weak acids of the carboxylic type. Usually also, the ethylenically unsaturated acid itself will be essentially the sole added acid, in amounts corresponding to 3-4 molecules for each chromium atom in the system, more usually about 3.3 moles per chromium. It should be noted that the dichromates described above exert an acid reaction in water; for example the pH of 5% by weight solution of $Na_2Cr_2O_7$ is about 3.5. Also, water, saturated with respect to commercial tall oil acid, has a pH of about 3.5. It is apparent then that the reaction mixture is initially quite acidic, and may even have a pH as low as 1-2. However, the indicated quantities of materials employed in this process provide for built-in pH control in the final reaction mixture, owing to the inherent acid-buffering capacity of the carboxylate ions generated by such process. As a result, the pH of the final reaction mass is generally in the range of 4.5-6.5. The preferred pH range is about 5-6 for the final product. If necessary, the pH of the final reaction mixture can be adjusted to this range in the normal manner by the addition of an acid or a base, as required. The use of controlled amounts of acid, i.e. the proportions defined above, provides for the formation of the Cr(III) carboxylate product of the reaction.

Under the conditions illustrated in Equation 1, the trivalent chromium accumulates substantially completely in the form of a water-insoluble, oil-soluble phase comprised of trivalent chromium carboxylate $(RCO_2)_3Cr$, while the alkali metal and alkaline earth metal ions accumulate predominantly in the form of an oil-insoluble phase. Any undesired alkali metal and alkaline earth metal carboxylate contamination of the trivalent chromium product may be decreased simply by water-washing the product.

The invention also provides for the production of oil-soluble trivalent chromium carboxylate compositions which contain minor but significant proportions of calcium soap. Such Cr(III) and Ca combination is especially effective to increase the electrical conductivity of distillate hydrocarbon fuels when employed in conjunction with a dipolar additive such as lecithin, as more particularly disclosed in British Patent No. 749,898. In this aspect of the process of this invention, there may be employed methanol or other alcohol as described above, e.g. a long chain primary alcohol reducing agent, i.e. having 10 to 22 carbons, preferably 12 to 18, such as axotridecanol, 2-hexyldecanol, or oleyl alcohol, which on oxidation forms oil-soluble soaps of both calcium and chromium, the result being the production of mixtures of chromium and calcium soaps, as illustrated in Equation 2, wherein $R'CH_2OH$ stands for oleyl alcohol and $R'CO_2H$ stands for oleic acid,



Where the R' groups are different, still different mixtures will be produced.

It will be noted that long chain saturated alcohols, when used as reducing agent, will form long chain saturated carboxylate groups which will appear in the salt products of Equations 1 and 2 above, randomly distributed amongst the unsaturated groups. Also, as indicated earlier, the starting fatty acid composition may sometimes have up to about 10 mole percent of the saturated analogs, e.g. the tall oil acids normally contain 3-6 percent saturated acids, which will appear in the salt product. In view of the

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above and the stoichiometry of the process represented by Equation 1, it will be apparent that the Cr(III) carboxylate product of this invention may contain up to about 30 mole percent, usually no more than about 10 mole percent, saturated carboxylate groups which do not seriously impair the utility of the product.

As indicated in Equation 1, water is normally a product of the oxidation reduction. While none need be added to the reaction mixture, water or other non-oxidizable inert diluent may be added if desired to facilitate the mixing of the reactants, provide a means for controlling the reaction temperature, or aid in the separation of the reaction products. Diluents which are suitably inert under the reaction conditions and which serve to provide the Cr(III) carboxylate product of reaction in the form of an easily handled liquid product are the normally liquid hydrocarbon and chlorinated hydrocarbon solvents, exemplified by benzene, toluene, ethylbenzene, the xylenes, chlorobenzene, o-dichlorobenzene, heptane, and kerosene, particularly the aromatic hydrocarbon solvents. When used, sufficient of the solvent is employed to dissolve the Cr(III) carboxylate product and preferably to provide a concentrate comprising 25%-75% by weight of the Cr(III) carboxylate, i.e. from about 0.25 to about 3 parts by weight of solvent for each part of Cr(III) carboxylate which theoretically will be produced from the amount of dichromate employed.

Broadly, the temperature of the reaction mixture may vary from room temperatures, i.e. about 25° C., to about 100° C., depending on the reducing agent and the degree of acidity of the reaction mixture. Reaction starts at about 25° C. with methanol as the reducing agent. In the preferred embodiments, temperatures of from about 60° C. to about 90° C. are employed and provide reasonably rapid reaction with a minimum formation of by-products.

The process of this invention comprises essentially the steps of (1) forming a mixture of the water-soluble hexavalent chromium compound (sodium dichromate), the reducing agent to produce Cr(III) (methanol), the water-insoluble unsaturated fatty acid (tall oil acid) and, optionally, an inert solvent (xylene) for the Cr(III) carboxylate to be produced, (2) heating the mixture with agitation until the reaction is completed, and (3) recovering a water-insoluble oil-soluble organic product comprising the Cr(III) carboxylate.

In the absence of a diluent solvent, the Cr(III) carboxylate is obtained as such, often as a viscous oil or a low-melting solid. With diluent solvent present, the Cr(III) carboxylate is obtained as a solution therein, a preferred form since the Cr(III) carboxylates are conveniently handled and, if necessary, further purified in such form, preferably in industrial xylene solvent.

It has been recognized in the art that, when heavy metal soaps of long chain fatty carboxylic acids are prepared in the presence of sodium salts, as for example in the metathesis of a sodium soap of the acid with a halide salt of the heavy metal, sodium soap adheres to the product and is difficult to remove. It has been found possible to minimize such contamination of the Cr(III) carboxylates of this invention by washing them with water. Emulsification tendencies can be controlled by adding to the wash water, before or after the extraction, a water-soluble weakly acidic ammonium salt of a strong mineral acid, e.g. ammonium chloride, ammonium phosphate or ammonium sulfate. From about 2% to about 10% by weight, usually about 5%, of the ammonium salt based on the wash water generally suffices for sharp phase separations. Such wash procedure, which is normally conducted on a hydrocarbon solution of the Cr(III) carboxylate product of the reaction, and at elevated temperatures, from about 70° C. to about 90° C., is highly effective to dissolve and remove alkali soaps without hydrolyzing the Cr(III) carboxylate and creating troublesome emulsions. The washed solutions may be dried in the usual manner, for example, by azeotropy or by filtering through or stor-

ing over a desiccant. By azeotropy is meant boiling out the water with a water-immiscible volatile solvent, normally a hydrocarbon such as benzene, toluene, xylene, heptane, iso-octane, or the like.

In order to more clearly illustrate this invention and the advantageous results obtained thereby, the following examples are given, wherein the quantities employed are in parts by weight except as specifically indicated otherwise.

Example 1

Twenty-five parts of sodium dichromate dihydrate (0.084 mole), 8 parts of methanol (0.250 mole, corresponding to a 100% molar excess), 160.8 parts of "Acintol" D (0.546 mole of distilled tall oil consisting essentially of $\frac{1}{3}$ oleic acid, $\frac{1}{3}$ linoleic acid and $\frac{1}{3}$ rosin acid) and 145 parts of industrial xylene (boiling range 137.2–140.5° C.) were mixed and heated under agitation at $65 \pm 5^\circ$ C. for 20 hours in a reflux reactor. The acid-dichromate quantities correspond to a molar ratio of H^+ to Cr of 3.25 to 1. The pH of the starting mixture was about 3.5, that of the final mixture about 6. The reaction mixture was then heated to drive out the water of reaction as the xylene azeotrope, temperatures up to 146° C. being reached, and then filtered through "Hyflo Super-Cel," a diatomaceous earth which is known as a "Celite" filter aid, to yield 348.2 parts of xylene solution containing 2.81% weight (100% yield) of chromium in the form of Cr(III) tallate and 0.55% weight of sodium, presumably in the form of a soap. The chromium content corresponds to a 47.6% weight solution in xylene of trivalent chromium tallate.

The sodium content of the product may be decreased to less than 0.1% weight by extracting the xylene concentrate 3 times at about 80° C. with an equal volume of water, adding after each wash 5% weight of ammonium chloride based on the water to break the emulsion. The xylene solution of the Cr(III) tallate is then dried by azeotropy as above.

Substantially the same product is formed when, in the above procedure, the xylene component is not added until after the 20-hour reaction period at $65 \pm 5^\circ$ C. In this case, the Cr(III) tallate is first obtained as a highly viscous liquid which is recovered and purified by extracting the reaction mixture with said xylene (145 parts), washing the extract with 100 part portions of distilled water, drying by azeotropy with xylene, and filtering.

Example 2

Two hundred and twenty-one parts of sodium dichromate dihydrate (0.742 mole), 46.4 parts of methanol (1.45 moles), 1,465 parts of "Acintol" D (4.82 moles), and 1,732 parts of industrial xylene solvent (boiling range 137.2–140.5° C.) are mixed and heated under agitation at $65 \pm 5^\circ$ C. for 16 hours. A "Celite" filter aid (145 parts of "Hyflo Super-Cel") is added and the mixture filtered at room temperature. The xylene solution is washed three times with 3,000 parts of 85° C. water for 30 minutes, 150 parts of ammonium sulfate being added to the wash water to break the emulsion after each extraction. Finally, the xylene layer is dried over 150 parts of anhydrous sodium sulfate, there being obtained 2,820 parts of xylene solution, analyzing 2.45% chromium (98.1% of theory, in the form of chromium(III) tallate) and 0.07% sodium. The above xylene solution consists essentially of a 42.3% weight concentrate of Cr(III) tallate.

Example 3

A. The procedure of Example 2 is repeated with oleic acid in place of said "Acintol" D in equimolar quantity to obtain Cr(III) oleate as a xylene concentrate in 93.3% yield.

B. Mixed Cr(III) carboxylates are obtained in excellent yields on employing an equimolar quantity of a 1:1 mixture of oleic acid and either "Acintol" D or "Acintol"

DLR, a specially distilled tall oil acid mixture having a low rosin acid content.

Example 4

In the procedure of Example 1, there are used 25 parts of sodium dichromate dihydrate, 25 parts of oxo-tridecyl alcohol (0.125 mole, no excess), a mixture consisting of 83.5 parts of "Acintol" DLR and 77 parts of oleic acid, and 145 parts of industrial xylene. After filtering, washing and drying as described in Example 1, there is obtained 279 parts of xylene solution containing 3.1% weight Cr(III). The yield is 98% recovery of Cr as Cr(III) carboxylate.

Example 5

33.3 parts of calcium dichromate trihydrate, 8 parts of methanol, 10 parts of water, 192 parts of "Acintol" DLR and 145 parts of xylene are mixed, and the mixture heated at $85 \pm 5^\circ$ C. for 18 hours. The reaction mass is dried, filtered, washed and re-dried as described in the previous examples. The resulting xylene solution, 297 parts, contains 3.1% weight Cr(III) and 0.1% Ca, corresponding to a 99% Cr yield as Cr(III) carboxylate.

Typical lots of "Acintol" D and of "Acintol" DLR used in the above examples have the following properties.

	"Acintol" D	"Acintol" DLR
Property:		
Acid Value.....	190	190
Saponification Value.....	193	196
Iodine Value (Wigs).....	164	159
Rosin Acids, Percent.....	32.0	21.0
Unsaponifiables, Percent.....	1.4	1.0
Fatty Acids Total, Percent.....	66.6	78.0
Fatty Acid Composition:		
Linoleic, Conjugated, Percent.....	9.0	18.0
Linoleic, Nonconjugated, Percent.....	37.0	34.0
Oleic, Percent.....	51.0	42.0
Saturated, Percent.....	3.0	6.0

Cr(III) salts of other ethylenically unsaturated monobasic fatty acids may be obtained by the process of this invention, illustrated in the above examples, by employing the corresponding unsaturated acids in place of the acids of the above examples in equimolar amounts.

It will be understood that the preceding examples have been given for illustrative purposes solely, and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be apparent to those skilled in the art that, subject to the limitations set forth in the general description, the materials, proportions, and conditions may be considerably varied without departing from the spirit or scope of this invention.

From the foregoing description, it will be apparent that this invention provides a new and improved process for making a class of valuable chromium(III) carboxylates economically and in high yields and in a high degree of purity from low cost readily available materials. Thereby, it is made economically practicable to employ such chromium(III) carboxylates as additives for petroleum distillate fuels. Accordingly, it will be apparent that this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises

(A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of

(a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;

- (b) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;
- (c) a reducing agent for said dichromate in an amount sufficient to completely reduce the chromium to Cr(III), said reducing agent being more readily oxidized than said ethylenically unsaturated fatty acid and having a standard oxidation potential in the range of minus 0.25 to plus 0.5 volt;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating the resultant Cr(III) carboxylate product from the by-product aqueous phase.
2. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) an acyclic primary alcohol of 1 to 22 carbon atoms which consists of carbon, hydrogen and oxygen, in an amount sufficient to completely reduce the chromium to Cr(III);
- (c) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating the resultant Cr(III) carboxylate product from the by-products aqueous phase.
3. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) a water-soluble, acyclic, saturated, primary alcohol of less than 8 carbon atoms which consists of carbon, hydrogen and oxygen, in an amount to provide from about 10% to about 100% molar excess over that which is theoretically required to reduce all of the chromium to Cr(III);
- (c) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 12 to 18 carbon atoms;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating the resultant Cr(III) carboxylate product from the by-product aqueous phase.
4. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium

- fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) from 1.5 to about 3 moles of methanol for each mole of dichromate;
- (c) about 3.3 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 18 carbon atoms;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating the resultant Cr(III) carboxylate product from the by-product aqueous phase.
5. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consist essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;
- (c) a reducing agent for said dichromate in an amount sufficient to completely reduce the chromium to Cr(III), said reducing agent being more readily oxidized than said ethylenically unsaturated fatty acid and having a standard oxidation potential in the range of minus 0.25 to plus 0.5 volt;
- (d) from about 0.25 to about 3 parts by weight of a normally liquid, inert solvent for each part of Cr(III) carboxylate theoretically to be produced, said solvent being at least one member of the group consisting of hydrocarbons and chlorinated hydrocarbons;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) carboxylate product in said solvent from the by-product aqueous phase.
6. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) an acyclic primary alcohol of 1 to 22 carbon atoms which consists of carbon, hydrogen and oxygen, in an amount sufficient to completely reduce the chromium to Cr(III);

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- (c) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;
- (d) from about 0.25 to about 3 parts by weight of a normally liquid aromatic hydrocarbon solvent for each part of Cr(III) carboxylate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) carboxylate product in said hydrocarbon solvent from the by-product aqueous phase.
7. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 60° C. to about 90° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) a water-soluble acyclic primary monohydric alcohol of less than 8 carbon atoms which consists of carbon, hydrogen and oxygen, in an amount sufficient to completely reduce the chromium to Cr(III);
- (c) from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 12 to 18 carbon atoms;
- (d) from about 0.25 to about 3 parts by weight of a normally liquid aromatic hydrocarbon solvent for each part of Cr(III) carboxylate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) carboxylate product in said hydrocarbon solvent from the by-product aqueous phase.
8. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
- (b) from 1.5 to about 3 moles of methanol for each mole of dichromate;
- (c) about 3.3 moles per chromium atom of a water-insoluble fatty carboxylic acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 18 carbon atoms;
- (d) from about 0.25 to about 3 parts by weight of xylene for each part of Cr(III) carboxylate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) carboxylate product in said xylene from the by-product aqueous phase.

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9. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 60° C. to about 90° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) sodium dichromate;
- (b) from 1.5 to about 3 moles of methanol for each mole of sodium dichromate;
- (c) from about 3 to about 4 moles per chromium atom of tall oil acids; and
- (d) from about 0.25 to about 3 parts by weight of a normally liquid aromatic hydrocarbon solvent for each part of Cr(III) tallate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) tallate product in said hydrocarbon solvent from the by-product aqueous phase.
10. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 60° C. to about 90° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) calcium dichromate;
- (b) from 1.5 to about 3 moles of methanol for each mole of calcium dichromate;
- (c) from about 3 to about 4 moles per chromium atom of tall oil acids; and
- (d) from about 0.25 to about 3 parts by weight of a normally liquid aromatic hydrocarbon solvent for each part of Cr(III) tallate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) tallate-calcium soap product in said hydrocarbon solvent from the by-product aqueous phase.
11. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 60° C. to about 90° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- (a) sodium dichromate;
- (b) from 1.5 to about 3 moles of methanol for each mole of sodium dichromate;
- (c) about 3.3 moles per chromium atom of tall oil acids;
- (d) from about 0.25 to about 3 parts by weight of xylene for each part of Cr(III) tallate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) tallate product in said xylene from the by-product aqueous phase.
12. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises

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- (A) reacting, at a temperature in the range of about 60° C. to about 90° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- calcium dichromate;
 - from 1.5 to about 3 moles of methanol for each mole of dichromate;
 - about 3.3 moles per chromium atom of tall oil acids;
 - from about 0.25 to about 3 parts by weight of xylene for each part of Cr(III) tallate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III); and
- (C) separating a solution of the resultant Cr(III) tallate product in said xylene from the by-product aqueous phase.
13. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 25° C. to about 100° C., an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- at least one water-soluble dichromate of the group consisting of alkali metal dichromates and alkaline earth metal dichromates;
 - from about 3 to about 4 moles per chromium atom of a water-insoluble fatty carboxylate acid composition which consists essentially of at least one ethylenically unsaturated fatty acid of 10 to 22 carbon atoms;
 - a reducing agent for said dichromate in an amount sufficient to completely reduce the chromium to Cr(III), said reducing agent being more readily oxidized than said ethylenically unsaturated fatty acid and having a standard oxidation potential in the range of minus 0.25 to plus 0.5 volt;
 - from about 0.25 to about 3 parts by weight of a normally liquid, inert solvent for each part of Cr(III) carboxylate theoretically to be produced, said solvent being at least one member of the group consisting of hydrocarbons and chlorinated hydrocarbons;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III);
- (C) separating a solution of the resultant Cr(III) car-

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- boxylate product in said solvent from the by-product aqueous phase; and
- (D) washing the separated solution with water at a temperature in the range of from about 70° C. to about 90° C.
14. The process for making water-insoluble oil-soluble metal salts comprised essentially of trivalent chromium fatty carboxylates wherein the carboxylate radicals are predominantly unsaturated, which comprises
- (A) reacting, at a temperature in the range of about 60° C. to about 90° C. an acid mixture having a total acid concentration providing 3 to 4 equivalents of hydrogen ion per atom of chromium and consisting essentially of
- sodium dichromate;
 - from 1.5 to about 3 moles of methanol for each mole of sodium dichromate;
 - about 3.3 moles per chromium atom of tall oil acids;
 - from about 0.25 to about 3 parts by weight of xylene for each part of Cr(III) tallate theoretically to be produced;
- (B) maintaining the mixture under said reaction conditions until the chromium is substantially completely reduced to Cr(III);
- (C) separating a solution of the resultant Cr(III) tallate product in said xylene from the by-product aqueous phase;
- (D) washing the xylene solution with water at a temperature of about 80° C.; and
- (E) adding about 5% by weight of ammonium chloride to the wash water.

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