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PRODUCTION OF CHROMIC ACETYLACETONATE

Filed April 8, 1954

2 Sheets-Sheet 1

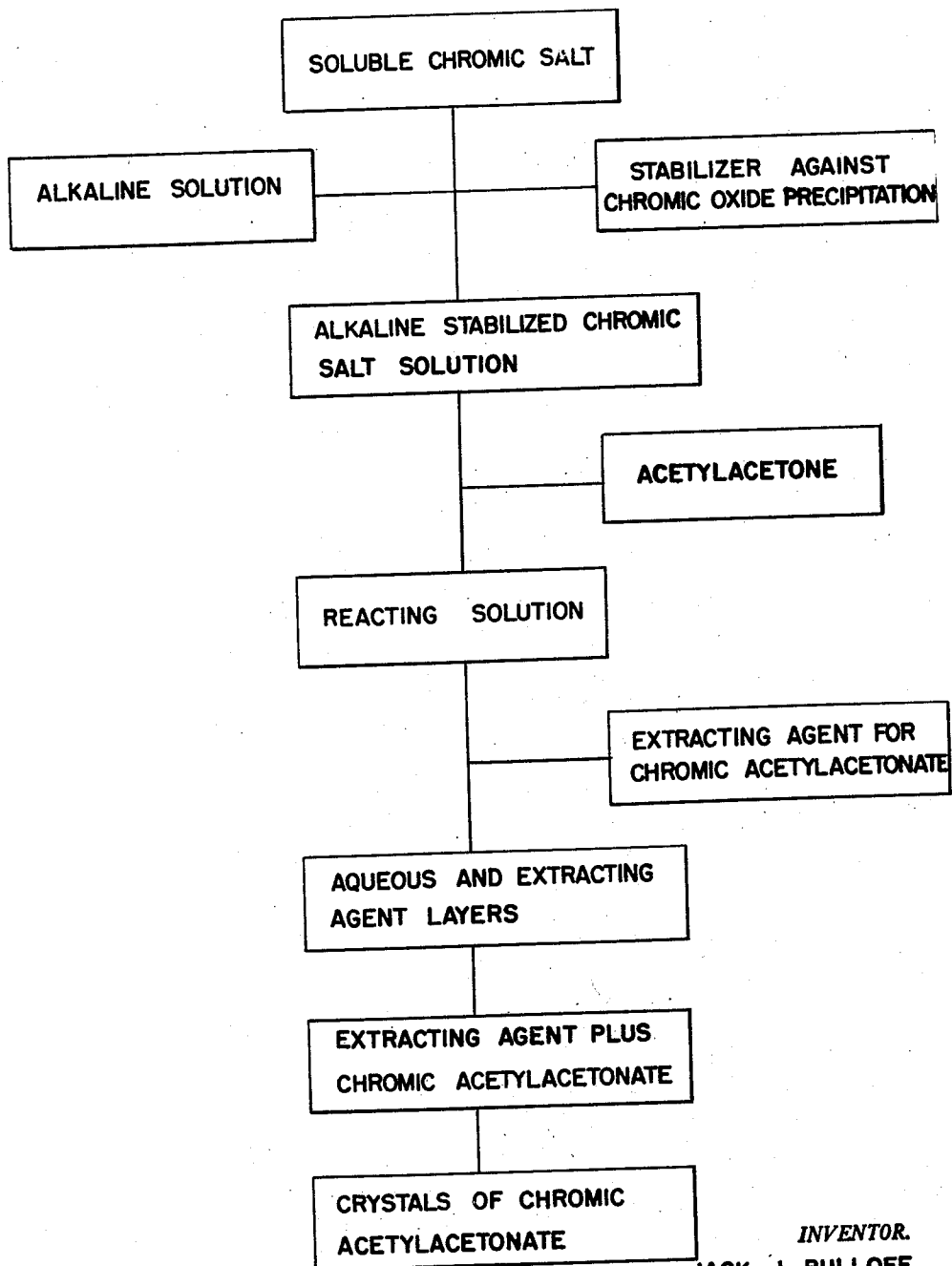


FIG.-1

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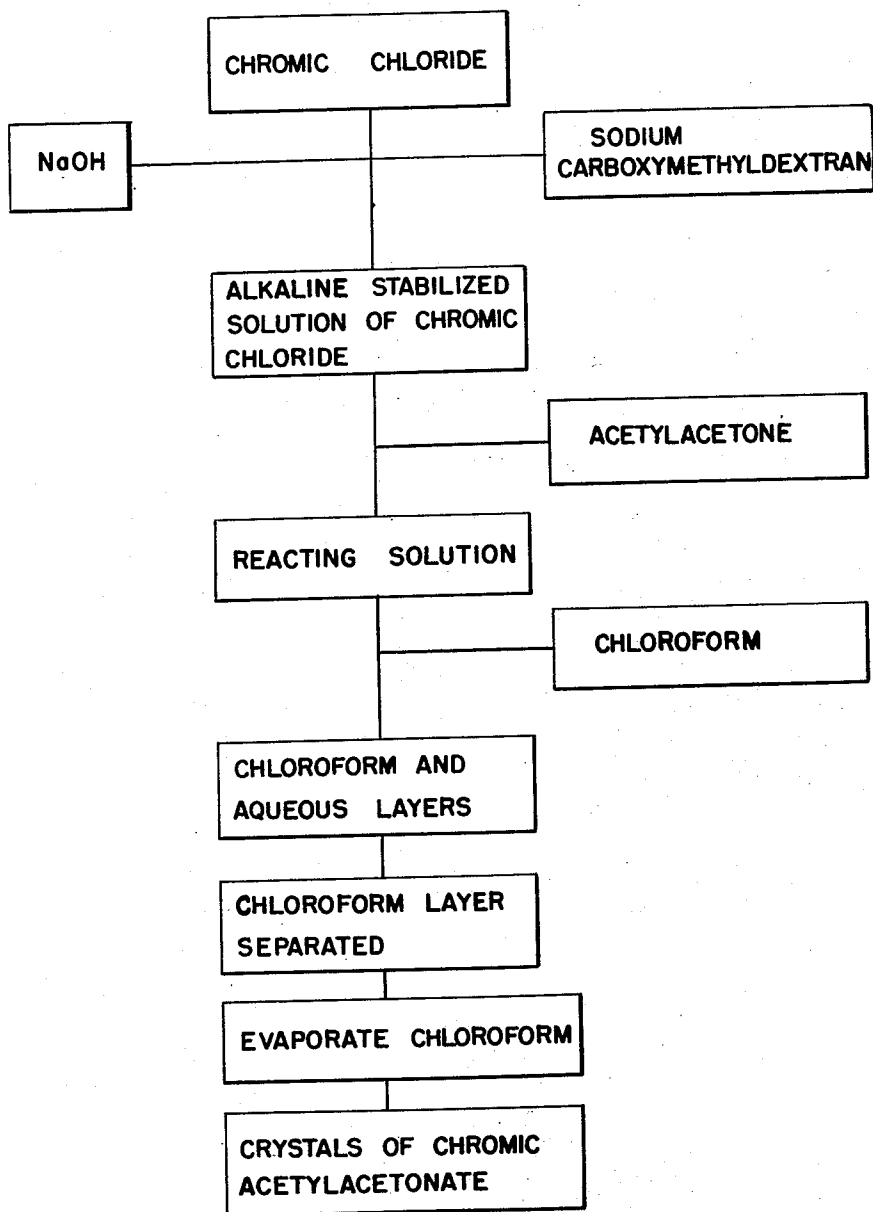


FIG.-2

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PRODUCTION OF CHROMIC ACETYLACETONATE

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11 Claims. (Cl. 260—438)

This invention relates to the production of chromic acetylacetonate.

Heat decomposable chromic salts have attained increasing importance in recent years but have been severely limited in industrial application due to the excessive cost of the heat decomposable materials which range in price to over a thousand dollars per pound and are even then frequently unavailable. Consequently the work with such material for the deposition of metal, black chromium oxides or green chromic oxide from the gaseous state has been confined primarily to a laboratory scale and in a number of known instances to small pilot plant production.

A useful compound for the deposition of chromium metal, or of the oxides, carbides, nitrides, or admixtures thereof, is chromium tri-acetylacetonate $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ but production thereof has been hindered because of the nature of the known processes which are sensitive and subject to the production of very low yields; co-precipitation of chromic hydroxide generally occasions the low yields, which may be avoided at least in part by the use of buffers or by the slow hydroxide addition to the reactants to keep the hydroxyl ion concentration low.

The employment of freshly precipitated hydrous chromium oxide in one process also aids in the avoidance of chromic hydroxide formation, but this procedure requires an excess of the expensive organic reagent, that is the acetylacetone, to attain complete conversion of the chromium to the acetylacetonate and is subject to losses should ageing of the hydrous oxide occur.

It is a primary object of this invention to provide an improved method for the production of chromium tri-acetylacetonate which method is not subject to the defects of prior art processes such as loss of activity upon ageing of hydrous chromic oxide, a usual starting material in known processes.

A further object of the invention is to provide a new method for the production of chromium tri-acetylacetonate which method does not require the use of buffered solutions and which method is effective to prevent the normal tendency of chromic salt solutions to precipitate hydrous chromic oxide upon standing or heating.

A still further object of the invention is to provide a method of producing chromium tri-acetylacetonate in a solution of extreme alkalinity wherein the acetylacetone is substantially completely converted to the acetylacetonate anion, and as such is present in a form miscible in water in contrast to those processes wherein the acetylacetone is present as an immiscible phase.

Still another object of the invention is to provide a chromium tri-acetylacetonate which is substantially free of chromic hydroxide.

An important object of this invention is to provide an aqueous reactant solution of chromic cations prepared from chromic salts of commerce, such as the chlorides, nitrates, sulfates, or chromic alums, by the addition thereto of hydroxyl anion in the form of a soluble hydroxide,

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the reactant solution being stabilized with a soluble carboxy methyl dextranate anion.

Yet another object of the invention is the provision of a method which is suitable for a continuous chemical process for the production of chromic acetylacetonate, the reaction mixture for the formation of the product being a single aqueous phase containing alkali cations, a stabilizer such as carboxy methyl dextranate in small quantity, chromic cations and acetylacetonate anions, all of which are non-extractable by organic solvents, the chromic acetyl acetone itself being extractable by organic solvents such as chloroform or ether.

The invention will be more fully understood by reference to the following detailed description and the accompanying flow sheet wherein:

The flow sheet of Figure 1 illustrates the generic aspect of the process; and

The flow sheet of Figure 2 sets out a specific procedure.

In the practice of the invention a chromic salt, preferably chromic chloride, is added to an alkaline solution, which solution is stabilized against hydrous chromic oxide formation, then acetylacetone is added thereto. The acetylacetone may be added in stoichiometric quantities to combine with the chromium, although an excess of the acetone is not harmful though it increases costs. Thereafter a solvent, chloroform for example, is added to the mixture, which is preferably agitated to prohibit any tendency toward a precipitate formation.

The addition of the chloroform results in the formation of two layers, one slightly green and aqueous; and the other, the chloroform layer, violet red in color. The chloroform is the important layer as upon evaporation thereof violet crystals are produced; which upon resolution in fresh chloroform, ether or other solvent, and subsequent evaporation produces brilliant violet crystals of chromic acetylacetonate. The mother liquor from which these crystals are derived contains substantially pure chromic acetylacetonate and may be reconcentrated to secure more product.

The invention will be more fully understood by reference to the following specific example, which is set forth by way of illustration and not by way of limitation:

Chromic chloride (CrCl_3) in a 5 percent aqueous solution (.02 mol equals 3.6 grams) was treated with a 10 percent solution of sodium hydroxide, which alkaline solution itself contained 1 percent by weight of sodium carboxy methyl dextran. This latter compound is a particularly efficient stabilizer for chromic salts in alkali solution—normally chromic salts upon standing in alkaline solution deposit increasing amounts of hydrous chromium oxide, and when heated to boiling such solutions of chromium salts quickly deposit their entire chromium content; however stabilization by the addition of agents, such as the carboxy methyl dextran referred to above, inhibits this tendency to deposit hydrous oxide. However upon addition of the alkaline solution to the solution of the chromium salt there will be noted that a slight precipitate generally first tends to occur, which readily redissolves if the solution of chromium salt is merely slightly stirred during the addition of the alkaline agent.

To the solution as formed acetylacetone was added (0.06 mol) and thereafter about 25 cc. of chloroform was admixed. After shaking, the chloroform layer and an aqueous layer separated, the chloroform layer being violet red and the aqueous solution faint blue green. The chloroform layer was decanted from the aqueous layer and then evaporated to form violet crystals. Examination showed the presence of about 0.02 mol of chromic acetylacetonate in the substantially pure violet crystal product.

Tests on the violet crystals produced by the evaporation of the chloroform layer which formed in the reaction solution were conducted to determine the characteristics

of the crystals. It was first noted that the initial crystals when heated in vacuum volatilized completely, redepositing as a red violet crystal. Vapors of the crystals when directed onto a hot ceramic under vacuum conditions deposited a black material, which material on heating in air became green in color and proved to be chromic oxide.

Pyrolysis of the vapors in the presence of a very small amount of air also yielded green chromic oxide. Heating the violet crystals in an excess of air resulted in combustion and the formation of a dark residue, which residue was analyzed and found to have a composition of substantially 1 Cr_2O_3 per 2 $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$.

Recrystallization of the violet crystals in ether or chloroform yielded violet crystals of somewhat increased brilliance. Mother liquor evaporation to drive off the ether or chloroform yielded the acetylacetonate of chromium.

Analysis of the aqueous layer from the original reaction solution showed that substantially no chromium remained unreacted.

While I prefer to use sodium hydroxide as the alkaline agent, other alkalies such as potassium hydroxide or any of the monovalent alkalies, are equally suitable; also sodium carbonate in about a 10 percent by weight solution may be employed if desired together therewith.

The sodium carboxyl methyl dextran is the most effective stabilizing agent which I have found as there is substantially no loss of chromium due to hydrous chromic oxide formation, and accordingly the chromium and acetylacetonate may be reacted together in stoichiometric quantities. Other carboxy methyl dextrans of the alkali metals may be employed with equal facility. Other stabilizing agents such as sodium carboxy methyl cellulose may be employed at risk of loss of some yield, because films form due to the high viscosity of the requisite stabilizing agent.

The chromic salt need not be the chloride, but other salts such as the nitrate may be utilized, the only requirement being that the anions form soluble compounds in the reaction. Further it is not necessary that the reaction take place in aqueous solution, for alcohol-water mixtures may be substituted for example, although there is no advantage to such, and in fact the cost factor results in a material disadvantage. As already noted ether and chloroform each are suitable for the practice of the invention, it being only necessary that the solvent employed be capable of being separated from the aqueous or alcoholic solution with the chromic component therein.

With respect to the product of the invention the same is free of contaminants including chromic oxide and will volatilize completely when heated in vacuum. When heated in the open air the product undergoes combustion giving off fumes which when collected on a cold metal plate are bright green having the composition Cr_2O_3 . Heating in air as noted hereinbefore results in some residue however due to formation of difficultly volatilizable oxides and carbonization, but this is not a detriment to the use of the compound for it is customary practice to employ vacuum conditions in gas plating work—that is the deposition of metals from the gaseous state.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. The method of producing chromic acetylacetonate which comprises reacting a solution of a soluble chromic salt with acetylacetone in an alkali medium stabilized with a carboxy methyl dextran of an alkali metal against hydrous chromic oxide precipitation.

2. The method of producing chromic acetylacetonate which comprises reacting stoichiometric quantities of a soluble chromic salt and acetylacetone in an alkali solution stabilized with a carboxy methyl dextran of an alkali

metal against hydrous oxide precipitation to produce chromic acetylacetonate.

3. The method of producing chromic acetylacetonate which comprises reacting a soluble chromic salt with acetylacetone in an alkaline medium stabilized against hydrous oxide precipitation with a soluble salt of carboxy methyl dextran, extracting the chromic acetylacetonate formed, and evaporating the extracting medium to form crystals of chromic acetylacetonate.

4. The method of producing chromic acetylacetonate which comprises reacting a soluble chromic salt with acetylacetone in an alkaline medium stabilized against hydrous oxide precipitation with sodium carboxy methyl dextran, extracting the chromic acetylacetonate formed with chloroform, decanting the chloroform layer produced, and evaporating the chloroform to form crystals of chromic acetylacetonate.

5. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with a water soluble salt of carboxy methyl dextran against chromic oxide precipitation, chromic chloride and acetylacetone, adding a preferential solvent for chromic acetylacetonate to the aqueous alkaline medium, removing said solvent from said medium, and evaporating the solvent to form crystals of chromic acetylacetonate.

6. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with sodium carboxy methyl dextran against chromic oxide precipitation, chromic chloride and acetylacetone, adding a preferential solvent for chromic acetylacetonate to the aqueous alkaline medium, removing said solvent from said medium, and evaporating the solvent to form crystals of chromic acetylacetonate.

7. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with sodium carboxy methyl dextran against chromic oxide precipitation, chromic nitrate and acetylacetone, adding a preferential solvent for chromic acetylacetonate to the aqueous alkaline medium, removing said solvent from said medium, and evaporating the solvent to form crystals of chromic acetylacetonate.

8. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with a soluble salt of carboxy methyl dextran against chromic hydroxide precipitation, stoichiometric quantities of a water soluble chromic salt and acetylacetone, adding chloroform to the solution to extract the chromic acetylacetonate formed, separating the chloroform and aqueous layers, and evaporating chloroform from the acetylacetone to produce crystals of the chromic acetylacetonate.

9. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with a soluble salt of carboxy methyl dextran against chromic hydroxide precipitation, stoichiometric quantities of a water soluble chromic chloride and acetylacetone, adding chloroform to the solution to extract the chromic acetylacetonate formed, separating the chloroform and aqueous layers, and evaporating chloroform from the acetylacetonate to produce crystals of the chromic acetylacetonate.

10. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with a soluble salt of carboxy methyl dextran against chromic hydroxide precipitation, stoichiometric quantities of a water soluble chromic nitrate and acetylacetone, adding chloroform to the solution to extract the chromic acetylacetonate formed, separating the chloroform and aqueous layers, and evaporating chloroform from the acetylacetonate to produce crystals of the chromic acetylacetonate.

11. The method of producing chromic acetylacetonate which comprises reacting, in an aqueous alkaline medium stabilized with a soluble salt of sodium carboxy methyl

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dextran against sodium hydroxide precipitation, stoichiometric quantities of a water soluble chromic chloride and acetylacetone, adding chloroform to the solution to extract the chromic acetylacetonate formed, separating the chloroform and aqueous layers, and evaporating chloroform from the acetylacetonate to produce crystals of the chromic acetylacetonate.

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