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PRODUCTION OF CHROMIUM AMMONIUM CHLORIDE COMPLEXES

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The invention relates to the electrodeposition of chromium and particularly to a method for producing a complex chromium compound of the purpeo and luteo type suitable for electrodeposition of metallic chromium.

Although luteo and purpeo chromium compounds are known, up to now there is no reference in the literature that metallic chromium was deposited from such compounds by electric current.

To any one skilled in the art it is known that the chromium purpeo and luteo compounds are chemical combinations of tri-valent chromium with coordinated valencies as shown by Werner's theory.

It is also known that the electrodeposition of metallic chromium in spite of all attempts was not a practical success up to the present time. By using the complex chromium ammonium combinations and by observing certain rules indicated hereinafter in producing such complex chromium ammonium combinations the metallic chromium of the tri-valent type may be easily extracted and deposited electrochemically in the same way as for instance silver is deposited from a complex sodium or potassium-silver-cyanide solution.

The difference between the electrodeposition of chromium metal from such a complex chromium ammonium combination and that from chromic trioxide is a basic one.

In chromic acid which is formed when chromic trioxide is dissolved in water the chromium ion is in combination with a radical represented as an anion, the kation being the hydrogen ion.

It is, therefore, necessary before isolating the metallic chromium from the aforesaid solution to bring or to transform the chromium ion from the anion group into the kation group to make the deposition for the chromium on the cathode possible.

This can be accomplished by the addition of certain agents, such as sulphuric acid or hydrofluoric acid, or certain fluorides. The purpose of these agents and the mechanics of their action is at present not very well understood.

The chromium metal deposited from such a solution is of the hexa-valent type, the deposition of which requires a much greater electrical energy than would be necessary for detachment of a trivalent chromium ion.

It is, therefore, evident that if the chromium ion would be originally in the kation group of a chromium chemical combination, such as is the case in the complex chromium ammonium combination, such a chromium ion would behave en-

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tirely differently under electric current than that of the chromic acid solution.

In other words such chromium ion would follow the electrochemical laws established for the more common metallic ions such as copper, nickel and others.

In practice this means that metallic chromium may be deposited from such type solutions with less energy, with better throwing power, and less erratic behavior of the electrolytic bath.

The complex chromium ammonium combination of the luteo and purpeo type were disclosed previously and are possible to be produced by widely different processes such as direct combination of chromic chloride with liquid ammonia (as described by Schlesinger) or by oxidation of chromous chloride as described originally by Joergensen, Christensen, and subsequently by Mellor.

However, whatever method of production is used the fact has been established that no prior method made possible the electrodeposition of metallic chromium from the aforementioned complex chromium combination.

The reason for this is, that a chromium ammonium complex combination of the purpeo or luteo type is produced from intermediate material such as chromic or chromous chloride, sulphate, etc., by either direct combination with ammonia such as described by Schlesinger or from chromic or chromous chloride, sulphate, etc., produced by an intermediate compound such as described by Joergenson, Mellor and others.

It is well known that chromic or chromous chloride or sulphate are not simple type combinations but that they are in fact a mixture of the α, β and γ sub-types.

It is, therefore, evident that if e. g. a commercial chromic or chromous chloride is taken as a base for production of a complex chromium ammonium combination, the resulting complex combination can never be of a uniform structure but will contain the characteristics of the intermediate combination.

Only then if a complex chromium ammonium combination is produced from chromic or chromous derivatives of uniform structure can we expect that such a complex chromium ammonium combination will be also uniform.

It is, therefore, imperative that a perfect control of production of the intermediate chromic or chromous chloride be exercised.

There are many factors entering in the production of such complex chromium ammonium combinations, such as temperature, time, im-

purities, and others which will be evident from the following description.

It is, therefore, the main object of my invention to provide a practical chemical combination and, consequently, a corresponding solution which will eliminate the disadvantages of the chromic trioxide solution and render electrodeposition of chromium more similar to metals such as copper, nickel, silver, etc.

It is a further object of my invention to utilize for the electrodeposition of chromium such chemical compositions or salts which, when dissolved in water, will disassociate electrolytically in such a way that the chromium ion is in the kation group.

It is evident that such a chemical composition will represent a complex metallic compound, in this case chromium compound or salt.

Werner's studies of such complex metallic ammonium compounds show the important fact that the electrolytic disassociation of $Cr(NH_3)_6Cl_4$ may be represented by an equation

$$[Cr(NH_3)_6]^{+++} \longleftrightarrow Cl_3^{---}$$

and the electrolytic disassociation of $Cr(NH_3)_5Cl_3$ is represented by the equation

$$[Cr(NH_3)_5Cl]\quad Cl_2=$$

It is evident from the above equations that in the above cases the positive chrome ion Cr^+ is in the complex kation group and must therefore in the electrolysis of the solution travel and be neutralized on the cathode, whereas the negative chlorine ion Cl^- is neutralized at the anode.

Of course, this assumption is strictly of a theoretical nature, which requires certain coordination with other factors in practice.

The following is the specification of an improved chemical process by which it is possible to obtain continually and most economically the complex chromium-ammonium compounds.

It is well known to the students of this group of complex compounds that the original production of them, as described in literature, is not only of the laboratory experiment type but also of a very erratic and inconsistent nature with no predictable results in the majority of cases. As previously mentioned the erratic nature is a consequence of the complexity of the intermediate product taken by previous workers at the starting point.

The known theoretical principle for the production of the complex chromium-ammonium compounds is quite simple. An inexpensive chromium salt, such as $K_2Cr_2O_7$ (potassium bichromate) is reduced by known means first to a chromic salt in solution such as $CrCl_3$. The chromic salt in turn is reduced to a chromous salt $CrCl_2$ in solution. This chromous solution is introduced into a mixture of ammonia (NH_3) solution with an excess of solid ammonium chloride (NH_4Cl).

This ammonia and ammonium chloride mixture with the introduced chromous chloride solution is kept for a certain time and without the access of air, in a closed container, where the oxidation of the bivalent chromium into a trivalent chromium takes place, by decomposing the water and acquiring the hydroxyl (OH) group, thus changing first into a basic complex chromium ammonium compound and, in turn, into a corresponding normal chromium ammonium compound, of the type $Cr(NH_3)_5Cl_3$ which is of rose color and thus known as chromium purpeo salt.

Joergensen showed that if the above specified

mixture is kept under a lowered temperature, say from zero to 19°, a different chemical compound is produced which deposits as yellow crystals and which can be represented by the formula

$$Cr(NH_3)_6Cl_3$$

so-called luteo chloride. He also showed that both of these complex compounds are soluble in water, but insoluble in alcohol, and therefore could be extracted, re-crystallized, and thus obtained in pure form from the ammonia-ammonium-chloride mixture.

The method of converting the basic material (in our case, potassium bichromate $K_2Cr_2O_7$) into the final complex chromium compound, including the necessary ammonium chloride (NH_4Cl) is as follows:

The integral part may be carried out by utilizing various well known reducing and oxidizing processes singly or in combination. For example, the first reduction of potassium bichromate ($K_2Cr_2O_7$) to chromic chloride ($CrCl_3$) in solution may be carried out according to the equation.

$$K_2Cr_2O_7+8HCl+3C_2H_5OH= 2KCl+2CrCl_3+3C_2H_4O+7H_2$$

utilizing ethyl alcohol and hydrochloric acid.

The resulting chromic chloride produced by this method is of very complex type as was proven by previous workers, and contain the sub-type groups of α chromic chloride, β chromic chloride, and γ chromic chloride, each of these sub-type chromic chlorides having different electro-chemical characteristics. If we convert chromic chlorides thus produced into chromous chloride utilizing for instance metallic zinc (Zn) as a reduction means according to the equation:

$$2CrCl_3+Zn=ZCr+ZnCl_2$$

We will obtain a blue solution of chromous chloride ($CrCl_2$) which chromous chloride is of a complex type following the characteristics of the subtypes of the chromic chloride.

It was established that the zinc utilised in the reduction of potassium bichromate in the presence of hydrochloric acid and converting said bichromate into chromous chloride is an important factor in influencing and determining not only the intermediate chromous chloride product but also the final complex chromium ammonium product.

It was further established that it is imperative to use two forms of metallic zinc in the reaction.

These two forms of metallic zinc are the solid and the mossy or porous zinc. It also was established that the ratio of quantities of these two forms of zinc is determinative for the speed of the reaction, the temperature under which the reaction takes place, and the length of time during which the reaction occurs. The speed and temperature of the reaction is determined by the mossy or porous form of the zinc, whereas the length or the duration of the reaction is determined by the solid zinc.

It is evident to one skilled in the art that the purity of both forms of zinc employed is also a determining factor in the production of the intermediate chromous chloride, and, therefore, it is necessary to use both forms of zinc free from impurities.

The producing of the intermediate chromous chloride is thus dependent upon the speed, the length of time of the reaction, and furthermore upon the temperature under which the reaction

is carried out, and which factors in turn are dependent from the form and purity of the zinc.

It is now evident that if such chromous chloride $CrCl_2$ is transferred without access of air into a mixture of ammonia-ammonium chloride, where the oxidation of the bivalent chromium (Cr^{++}) into a trivalent chromium (Cr^{+++}) takes place, the resulting chemical combination will not be a uniform complex chromium-ammonium combination but a mixture of complex chemical combinations following the characteristics of the subtypes of the starting material, in our case the chromic chloride $CrCl_2$.

It will be noted that with the chromous chloride ($CrCl_2$) solution is also transferred the zinc chloride ($ZnCl_2$) which was produced during reduction of chromic chloride ($CrCl_3$) with zinc.

This zinc chloride is very bothersome in the oxidation of the chromous chloride ($CrCl_2$) and also in the correspondent process of procuring the final complex chromium-ammonium.

It is true that it can be separated from the final complex chromium-ammonium compound to obtain a pure complex compound, but for the purpose of using such a complex chromium-ammonium compound in electrodeposition of chromium metal, I find it imperative to separate the zinc chloride ($ZnCl_2$) by a separate chemical process interpolated in my method.

I also find it necessary in my method of continuous production of the complex chromium-ammonium compounds to coordinate the various chemical processes utilized in converting the raw material (potassium bichromate) into the final product as follows:

Finely granulated potassium bichromate ($K_2Cr_2O_7$) is placed into a large container with an excess of zinc (Zn), and diluted hydrochloric acid (HCl) is allowed to run into the mixture. In my experiments I found that the hydrochloric acid should be diluted in the ratio of 2:3 and should be preheated to an optimum temperature between 45 and 50° C. A violent reaction takes place in the first few minutes, which reduces the potassium bichromate first into a deep green solution of chromic chloride ($CrCl_3$). Then the reaction quiets down, and in ten to fifteen minutes the reaction is finished and the solution turns into a clear blue color, namely that of chromous chloride ($CrCl_2$). This solution, as previously mentioned, contains also the zinc chloride ($ZnCl_2$).

The excess of developed hydrogen (H) during the reaction is carried away through a water seal to protect the chromous chloride ($CrCl_2$) solution from oxidation by air.

It is imperative that this reaction is carried out without the least trace of atmospheric oxygen, therefore, it must be carried out in an inert atmosphere such as carbon dioxide (CO_2), nitrogen (N), hydrogen (H) or any other inert gas, which inert gases must be of the highest purity produced by corresponding washing. Any impurities in the atmosphere in which the aforesaid reaction is taking place will have an effect upon the characteristic of the chromic or chromous chloride so produced. It is further important that the reaction temperature during the reduction is kept constant. It is further important that all the impurities from the reaction entering factors are eliminated especially the impurities in the metallic zinc.

In the course of my experiments I also found out that two types of metallic zinc should be used: The mossy type and the solid type. The

reason for this is, that if only one type of zinc is used the reaction will be either too fast or too slow, thus affecting the characteristic of the yield.

It is evident that after the aforementioned reduction there is a mixture of chromous and zinc chloride in the reaction chamber.

The next step in the processing of the blue chromous chloride ($CrCl_2$) containing the zinc chloride ($ZnCl_2$) consists of bringing the blue solution to contact with a saturated solution of sodium acetate

$$(NaC_2H_3O_2.3H_2O)$$

This operation is also carried out in an atmosphere of carbon dioxide or other inert gas. A red precipitate of chromous acetate,

$$Cr_2(C_2H_3O_2)_6.2H_2O$$

is the result, the zinc chloride remaining in the solution.

After the precipitate settles down the supernatant liquid containing the zinc chloride and other soluble impurities is decanted and the precipitate is washed under agitation with water saturated with carbon dioxide (CO_2) and water acidified with acetic acid ($CH_3.COOH$).

The red chromous acetate, $Cr_2(C_2H_3O_2)_6.2H_2$, is practically insoluble in such washing water and, therefore, it may be entirely separated from all impurities, particularly zinc just by repeated washing with acidified and carbon dioxide (CO_2) saturated water.

After the final washing the precipitate is allowed to settle, the washing water decanted, and the container filled with carbon dioxide (CO_2) or other inert gas. In this inert atmosphere concentrated hydrochloric acid (HCl) is allowed into the container, which acid dissolves the precipitate, forming a blue solution of chromous chloride ($CrCl_2$) without any zinc or metallic impurities. The zinc may be recovered from the supernatant liquid and from the wash-water by precipitation with alkali carbonates as a by-product.

It is important that the aforementioned washing of the chromous acetate and the consequent dissolving thereof in hydrochloric acid is shielded from any traces of oxygen, for it is well known that chromous chloride is extremely sensitive to oxygen.

The pure solution of chromous chloride ($CrCl_2$) may be again stored in quantities in an atmosphere of carbon dioxide (CO_2) or other inert gas, or it may be processed further without delay.

A portion of the pure chromous chloride ($CrCl_2$) solution is placed in a container, the temperature of which is brought up to 68° C. During the application of heat to the container, the same is evacuated and the concentration of the chromous chloride ($CrCl_2$) solution takes place and is carried to the point when the crystallization starts to take place.

In my experiments I found out that a much better method than the use of vacuum is to connect the vessel containing the chromous chloride and to which the heat is applied with a source of pure nitrogen gas and to provide the outlet of the vessel with a water seal thus carrying out the concentration of the solution in an inert atmosphere.

When the proper construction of the chromous chloride ($CrCl_2$) solution is reached the same is transferred in an atmosphere of nitrogen (N) or hydrogen (H), but not of carbon di-

oxide (CO_2), into a vessel containing a mixture of solid ammonium chloride (NH_4Cl) and concentrated ammonia water.

The vessel is sealed with a water seal and placed in a constant temperature water bath. The liquid in the vessel, which has a blue color after the transfer, turns gradually depending upon the temperature into a deep red color and hydrogen is developed, escaping through the water seal, which seal also prevents the oxygen of the air from coming in contact with the mixture. When the development of hydrogen (H) ceases, the process is ended and the liquid filtered into a storage tank or directly into the crystallization pans.

The ammonia chloride crystals remaining in the vessel are washed once or twice with cold water and the resulting reddish liquid stored in a separate tank. This liquid contains mostly the complex chromium ammonium salts of the luteo and roseo type, depending, as previously said, on the temperature maintained during the oxidation process in the water bath. It may be added to the mother liquid or it may be crystallized separately.

The crystallization pans are placed in a dust free room and in a current of dry pre-heated air. The crystallization begins very shortly and is carried up to the point when all the liquid is evaporated and dry flakes of violet color are left in the crystallization pans.

These crystalline flakes dissolve easily in cold water and re-crystallization process may be employed. The composition of these crystals may be formulated as follows:

Chromium pentamino trichloride (purpeo)

$(Cr(NH_3)_5Cl_3)$

Chromium hexamino trichloride (luteo)

$(Cr(NH_3)_6Cl_3)$

Ammonium chloride

(NH_4Cl)

In carrying out the process reference has been made to complex chromium compounds of the purpeo and luteo type which theoretically as most suitable material for the electrodeposition of chromium.

During the experiments I found out that only the purpeo type is suitable for electrodeposition and consequently that it is necessary to promote the formation of the purpeo type and prevent the formation of the luteo type during the reaction of chromous chloride with ammonia in the presence of ammonium chloride.

This can be very easily achieved by close control of the temperature of the reacting solutions. It is well known that if the temperature is allowed to drop under 18° C. the formation of the luteo predominates. If, however, the reacting solution is kept above 18° C. the formation of the purpeo type predominates.

I further found out that the optimum temperature is between the limits of 25° C. to 30° C.

It is furthermore important that this temperature be kept constant during the entire reaction time.

While the specification describes a compound suitable for electrodeposition of chromium and the method of producing such compound, numerous changes in replacing the anion group by a different radical may be made without departing from the invention.

I, therefore, claim my invention as broadly as the state of the art permits.

I claim:

1. The method of producing a complex chromium ammonium chloride combination suitable for electrolytic deposition of chromium metal, including the steps of converting potassium bichromate in the presence of hydrochloric acid by specific reduction agents comprising predetermined quantities of zincs of the solid and mossy or porous type to a bivalent chromium chloride compound, converting further said bivalent chromium chloride compound into a bivalent chromium acetate compound, separating said acetate compound by washing and filtration from the solution and oxidising said bivalent compound to a trivalent complex chromium in reaction with ammonia, ammonium chloride and water and separating the ammonium chloride crystals from the resulting product by repeated washings.

2. The method of producing a complex chromium ammonium chloride combination suitable for electrolytic deposition of chromium metal, including the steps of converting potassium bichromate by bringing said bichromate in chemical reaction with hydrochloric acid and a mixture of chemically pure solid and porous zinc particles to a bivalent chromium chloride compound, converting further said bivalent chromium chloride compound into a bivalent chromium acetate compound, separating said acetate compound by washing and filtration from the solution and oxidising said bivalent compound to a trivalent complex chromium in reaction with ammonia, water, and ammonium chloride, said steps being carried out in accordance with predetermined temperature, time and speed of reactions and separating the ammonium chloride crystals from the resulting product by repeated washings.

3. The method of producing complex chromium ammonium chloride combinations suitable for electrolytic deposition of metallic chromium, including the steps of placing potassium bi-chromate into a mixture of hydrochloric acid and a mixture of solid and porous metallic zinc, bringing the resulting chromous chloride and the zinc chloride in reaction with a saturated solution of sodium acetate thus removing from the precipitate all residual zinc compounds, and separating the precipitate of chromous acetate from the solution by filtration, adding hydrochloric acid to convert the formed chromous acetate into pure chromous chloride, heating the chromous chloride to concentrate it, mixing it with a mixture of solid ammonium chloride and concentrated ammonia water, and crystallizing the liquid after the oxidation free from access of air of the mixture is completed and separating the ammonium chloride crystals from the resulting product by repeated washings.

4. The method of producing complex chromium ammonium chloride combinations suitable for electrolytic deposition of chromium metal, including the steps of placing finely granulated potassium bichromate into a mixture of hydrochloric acid and a mixture of solid and porous metallic zinc acting as a reducing agent bringing the resulting chromous chloride and zinc chloride in reaction with a saturated solution of sodium acetate thus removing from the precipitate all soluble zinc compounds, and separating the precipitate of chromous acetate from the solution by filtration, adding hydrochloric acid to obtain pure

chromous chloride, heating the chromous chloride to concentrate it, mixing it with a mixture of solid ammonium chloride and concentrated ammonia water, and crystallizing the liquid after the oxidation free from access of air of the mixture is completed and separating the ammonium chloride crystals from the resulting product by repeated washings.

5. The method of producing complex chromium ammonium chloride combinations suitable for electrolytic deposition of chromium metal, including the steps of placing potassium bi-chromate into a mixture of hydrochloric acid and a mixture of solid and porous metallic zinc acting as a reducing agent, bringing the resulting chromous chloride and the zinc chloride in reaction with a saturated solution of sodium acetate in an atmosphere of inert gas thus removing from the precipitate all soluble zinc compounds, and separating the precipitate of chromous acetate from the solution by filtration, adding hydrochloric acid to obtain pure chromous chloride, heating the chromous chloride to concentrate it, mixing it with a mixture of solid ammonium chloride and concentrated ammonia water, and crystallizing the liquid after the oxidation free from access of air of the mixture is completed and separating the ammonium chloride crystals from the resulting product by repeated washings.

6. The method of producing chromium ammonium chloride combinations suitable for electrolytic deposition of chromium metal, including the

steps of converting intermediately an alkaline bichromate in the presence of hydrochloric acid and a mixture of constant ratio of solid and porous metallic zinc to a trivalent chromic chloride and subsequently into a bivalent chromous chloride, converting said chromous chloride into a water insoluble chromous acetate, eliminating impurities by repeated washing and separating the precipitate of chromous acetate from the solution by filtration, reconverting said chromous acetate to chromous chloride, introducing the pure chromous chloride into a mixture of solid ammonium chloride and ammonia water, subjecting said mixture to a constant temperature, and after the reaction is completed subjecting said mixture to crystallization and separating the ammonium chloride crystals from the resulting product by repeated washings.

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