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by

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Anhydrous Chromic Chloride

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(Abstract)

Anhydrous chromic chloride, $CrCl_3$, is not yet manufactured on the tonnage scale even though it has several potential industrial uses, owing to difficulties encountered in scaling up the known laboratory methods of preparation. These problems are reviewed in the present work, and criteria for an ideal process for the large-scale production of $CrCl_3$ are thus identified. A new low-temperature route to $CrCl_3$ is proposed that meets these criteria and is therefore suitable for commercial exploitation.

Introduction

Anhydrous chromic chloride, $CrCl_3$, a red-violet, non-hygroscopic compound of micaceous appearance melting at 1150 °C and subliming at 1300 °C (1), is essentially insoluble in water, mineral acids and alkalis. Readily solubilised in the presence of reducing agents such as zinc and hydrochloric acid, or chromous chloride, however, it is very different from the hydrous forms of chromic chloride (2) (3).

A number of large-scale uses for anhydrous chromic chloride have been investigated in some detail, but as $CrCl_3$ is not yet manufactured on the tonnage scale these uses are mostly potential rather than actual: for example, chromium hexacarbonyl, $Cr(CO)_6$, and organochromium compounds are often synthesised from $CrCl_3$ (2) (3), especially by way of the useful tetrahydrofuranate intermediate, $CrCl_3 . 4THF$, which is soluble in organic solvents. $CrCl_3$ is also known to catalyse the polymerisation of olefins (3), and is easily reduced to anhydrous, white chromous chloride, $CrCl_2$, with hydrogen at 600 °C (4) or by electrolysis in a molten salt bath (5); $CrCl_2$ is a powerful reducing agent.

The most important uses, however, probably relate to the preparation of chromium sponge and chromium powders for metallurgical use by the complete reduction of $CrCl_3$ (or $CrCl_2$) with hydrogen at about 800 °C(4) (6) or by electrolysis as above (5). In the presence of a suitable metal substrate the hydrogen-reduction 'chromising' process enables a diffusion coating of hard, corrosion–resistant chromium with low coefficient of friction to be obtained (7) (8) that overcomes certain problems associated with competing chromium electroplating processes (9). In particular, hexavalent electrolytic baths generate spent electrolyte streams requiring a two-stage effluent treatment process, and in addition release toxic chromic acid spray into the atmosphere above the electrolytic cell; trivalent electrolytic processes, on the other hand, incur 20 % higher capital and operating costs because they employ much lower current densities. Another way of obtaining coatings of chromium, by the thermal decomposition of bisbenzenechromium at 300 °C in vacuo, suffers the disadvantage of producing an impure coating containing as much as 0.3 – 10 % carbon (10).

Chlorination of Chromite

Attempts to develope an economically viable process for the manufacture of anhydrous chromic chloride have traditionally been based on the direct chlorination of chromite, a chromium-bearing mineral in the spinel group of widely varying composition usually in the range: $(Mg_{30-75}, Fe_{70-25\ mol\ \%}{}^{2+})\ O.\ (Cr_{40-50}, Al_{10-80}, Fe_{0-13\ mol\ \%}{}^{3+})\ {}_2O_3$ with $R^{2+}O\,/R^{3+}\,{}_2O_3 \doteqdot 1$ mol/mol. Indeed, the first patent for a process of this kind was granted as long ago as 1915 (11). Thereafter the possibility of utilising the large North American deposits of lowgrade chromite ore encouraged fairly rapid progress until the early 1930's, culminating in a major research programme at the US Bureau of Mines founded on a study of the chemical thermodynamics of chlorination in 1937 (12), and resulting in a report (13) detailing conditions in which the various oxide constituents of chromite could be chlorinated. A process whereby the $CrCl_3$ prepared by reacting chromite with carbon and chlorine gas could be reduced to chromium metal sponge with hydrogen was also suggested. At the same time the main problems associated with large-scale operations were identified: the formation of gaseous $CrCl_4$ with its inefficient use of chlorine; low rates of heat and mass transfer owing to the coating of ore particles with molten chromous, magnesium and calcium chlorides; the difficulty of separating $CrCl_3$ from other reaction products. Suggested ways of alleviating the problems included operating the reactor at higher temperatures than hitherto, using excess chlorine gas and mixing the finely divided ore with an inert carrier. The $CrCl_3$ was purified by distilling off volatile contaminants at 300–700 °C in a stream of anhydrous hydrogen chloride gas and leaching out involatile but soluble impurities with water. Apparatus for the separation of $CrCl_3$ from the mixture with $FeCl_3$ obtained by the complete chlorination of chromite at 900–950 °C, by differential condensation of the mixed vapours, has also been described (14) (15).

In spite of much effort, none of the high-temperature chromite chlorination processes studied to date have been employed commercially as a route to $CrCl_3$. In fact the authors of a brief review in 1959 (3) concluded that the problems associated with the chlorination of chromite were so intractable that processes based on pure chromic oxide were to be preferred. It was observed, moreover, that none of the earlier workers had published the chemical analyses of any the $CrCl_3$, products derived directly from chromite, Since then research has continued but usually with the more modest intention of upgrading chromite ore by the selective volatilisation of $FeCl_3$, for example in studies of the chlorination of Egyptian chromite ore (16) and synthetic oxides and spinels (17).

Chlorination of Pure Compounds of Chromium

The principle methods of preparing $CrCl_3$ were critically reviewed in 1931 and found to fall into three main groups (18):

$$Cr_2O_3 + Cl_2/C \overset{700/800\,^{\circ}C}{\rightleftharpoons} CrCl_3\ (g)$$

$$Cr_2O_3 + Cl_2/CCl_4 \overset{800\,^{\circ}C}{\rightleftharpoons} CrCl_3\ (g)$$

$$Cr + Cl_2 \overset{600\,^{\circ}C}{\rightleftharpoons} CrCl_3\ (g)$$

The condensed products obtained are generally hygroscopic and impure, containing water, chromous chloride and chromium oxychloride, but can be purified by distillation at 500 °C in a stream of dry chlorine gas containing a trace of carbon tetrachloride vapour. Indeed, the purification of $CrCl_3$ has often played an important role in the selection of preparative techniques. For example, $CrCl_3$ prepared according to the first of the above equations was re-sublimed in dry chlorine gas, dehydrated in a stream of chlorine gas containing CCl_4 vapour at 300 °C and de-gassed in vacuo before being considered suitable for thermal capacitance studies (19). Similarly, when using chlorine with a trace of CCl_4 vapour at 850–900 °C, repeated sublimation followed by annealing for several hours at 600–700 °C was apparently necessary before phase equilibrium studies could be carried out (20). Even with $CrCl_3$ prepared by the direct chlorination of 99.9 % pure chromium metal at 960 °C, re-sublimation in a stream of dry chlorine gas was required prior to preparing $CrCl_2$ (21).

Nevertheless a pilot plant has successfully produced $CrCl_3$, containing 0.08–0. 69 % carbon, by the direct chlorination of Cr_2O_3 / carbon pellets at 955–1040 °C using chlorine gas in 10 % excess of stoichiometric requirements (3). The product, however, was voluminous and difficult to handle. A flaky form of $CrCl_3$ condensed on cool surfaces, along with a fluffy form that condensed in the gaseous atmosphere: the bulk densities of the two forms of $CrCl_3$ product were only 0.5 and 0.1 kg/m^3 respectively.

Cr_2O_3 pellets containing water and carbon in 150 % excess of stoichiometric requirements have also been chlorinated in a large scale laboratory apparatus (22). The pellets, dehydrated at 300–350 °C, started reacting slowly at 600 °C but did not react rapidly until 950 °C. Upon being cooled to 400 °C in a stream of dry chlorine gas the $CrCl_3$ product was found to be of spectrographic purity.

The relative reactivity of annealed chromic oxide has also been investigated (23): chromic oxide annealed at 440 °C and 1000 °C and then chlorinated at temperatures up to 950 °C yielded 38 and 98 % $CrCl_3$ respectively; the amounts of $CrCl_3$ volatilised when chlorinating at 600, 850 and 950 °C were found to be 1 %, 36 % and 71 % respectively. As might be expected, the Cr_2O_3 prepared by annealing at 440 °C was slightly more reactive than that prepared at 1000 °C; this was especially so at the lower chlorinating temperatures.

An early general method for the preparation of metal chlorides by the action of carbon tetrachloride vapour on metal oxides is applicable to $CrCl_3$ at temperatures above 580 °C (24) (25). In the refined form of the technique (26), hydrated chromic oxide is dehydrated and chloridised with CCl_4 vapour at 620–630 °C (at higher temperatures carbon is formed); the volatilised $CrCl_3$ is condensed at 475–500 °C and purified by passing dry chlorine gas through the condenser until the product is cool. The yield obtained is generally only 65–70 % but the $CrCl_3$ produced is suitable for the preparation of bisbenzene chromium.

Dehydration of Hydrous Chromic Chloride

The thermal dehydration of hydrous chromic chloride leads to the formation of hydrolysis products such as CrOCl at 320 – 410 °C, and Cr_2O_3 at higher temperatures. $CrCl_3$ therefore cannot be prepared by the direct thermal dehydration of hydrous chromic chloride (26) (27).

Nevertheless, $CrCl_3$ has been prepared free from hydrolysis products by dehydration in the presence of: CCl_4 vapour for 8 hours at 300 – 650 °C (28) (29); carbonyl chloride, $COCl_2$, under reflux for 24 hours at 190 °C (30); sulphuryl chloride, $SOCl_2$, at a somewhat lower temperature (31); dry HCl gas for 12 hours at 140 °C (32). Quite apart from the slowness of these reactions, however, the physical properties of hydrous chromic chloride make the above processes unusually difficult to scale up: at about 150 °C the hydrous chromic chloride melts, and at higher temperatures it re-solidifies and swells until it occupies a volume many times larger than that of the original crystals.

Alternative methods of synyhesising $CrCl_3$ are also known: for example, chromic acid, CrO_3, can be refluxed with $SOCl_2$ at 150 °C with a small amount of ethanol, but the product contains 7 % sulphate and must be purified by sublimation (33); or chromyl chloride, CrO_2Cl_2, can be reacted at 750–850 °C with such reducing agents as carbonyl chloride, chlorohydrocarbons, or mixtures of chlorine with carbon monoxide or hydrocarbons. It should be noted, however, that in accordance with thermodynamic calculations, chromium metal and dry hydrogen chloride gas react at 900 °C to form not $CrCl_3$ but $CrCl_2$ (34).

Summary of Commercial Problems

The currently available processes for the production of anhydrous chromic chloride are both difficult and costly to scale up owing to three main problems:

When chromite is chlorinated directly the magnesium, calcium and silicon oxides generally present in the ore chlorinate in the reaction mixture to form a sticky, molten mass that coats the particles of chromite, thus both decreasing the rate of chlorination and increasing the difficulty of separating the $CrCl_3$ product.

Purification of the $CrCl_3$ product in the separation and recovery stages by re-sublimation, in vacuo or in a stream of dry chlorine gas, is recommended (34) for practically all the known methods of preparation. The differential condensation at high temperatures of the voluminous, flaky or fluffy, volatile solids is difficult to control efficiently (35).

The containment of highly corrosive gases at elevated temperatures remains a major engineering problem (35) (36). At wall temperatures above about 600 °C with hydrogen chloride gas, or above 500–550 °C with chlorine gas, only graphite/carbon (3) and refractory materials such as high purity alumina (37) (38) are suitable as materials of construction; fused silica is not a practicable material for large-scale units of equipment (39).

An Ideal Process

There would therefore appear to be a need for a new process for the large-scale production of anhydrous chromic chloride. Ideally, such a process would have the following attributes:

The chlorinating temperature would be below 525 °C, thus allowing nickel to be used as a material of construction (37) (39) and at the same time preventing volatilisation of the $CrCl_3$ product (in the absence of chlorine gas).

The raw material would be a cheap, primary or secondary chromium chemical, thus facilitating integration of the process into existing chromium chemical plants.

The chlorinating agent would not introduce any metallurgically undesirable impurities such as carbon, sulphur, iron or other heavy metals into the reaction system; nor would the special precautions required when handling such highly toxic gases as anhydrous chlorine, anhydrous hydrogen chloride or carbonyl chloride be necessary.

The chlorination reaction would be rapid and exothermic, and would make efficient use of the chlorine in the chlorinating agent.

There would be no chromium byproducts and the recovery of chromium would exceed approximately 96 %.

The $CrCl_3$ product would not require to be purified by sublimation.

There would be no environmentally damaging effluents.

Proposed New Process

On the basis of the above criteria, the low-temperature chlorination of active chromic oxide has been studied as a new route to anhydrous chromic chloride with potential for commercial exploitation (40). Further papers now being prepared will describe relevant aspects of the process in greater detail.

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Susuz Krom (III) klorür

(Özet)

Susuz krom (III) klorür, $CrCI_3$, çeşitli endüstriyel kullanım potansiyelleri olduğu halde, bilinen laboratuvar hazırlama yöntemlerinin, miktar arttırmada karşılaşılan güçlüklerden dolayı, henüz büyük miktarlarda üretilememiştir. Çalışmada bu güçlükler gözden geçirilmiş ve böylece $CrCI_3$'ün büyük miktarda ideal bir üretimi için kriterler (ölçüler) belirlenmiştir. Bu kriterleri karşılayan ve böylece ticari işletmelere uygun yeni bir düşük sıcaklık $CrCI_3$ yöntemi teklif edilmiştir.

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