THE DEPOSITION OF METALS FROM SOLUTION ON A DISPERSED PHASE

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Ivor John Grayson-Smith, M.A.
Department of Metallurgy,
Royal School of Mines,
Imperial College of Science
and Technology,
London, S.W.7.

ABSTRACT

New methods of depositing the metals chromium and aluminium from solution onto non-metallic solids have been developed to deposit these metals on single-crystal whiskers in order to form the strong bond between whiskers and metal which is essential for effective whisker-strengthening. Methods based on the chemical reduction of compounds of chromium and aluminium in solution have been unsuccessful.

Chromium has been successfully deposited by the thermal decomposition of a 10 per cent. solution of bisbenzenechromium in an equal-weight mixture of n-Octadecane and t-Stilbene, and by the thermal decomposition of a 10 per cent. solution of t-Stilbene chromium tricarbonyl in an equal-weight mixture of n-Octadecane and t-Stilbene, at temperatures above 300°C.

Aluminium has been deposited by the thermal decomposition of a 10 to 15 per cent. solution of di-isobutyl aluminium hydride in n-Octadecane at temperatures above 210°C.

In all cases adherent metal coatings have been formed on metallic and non-metallic surfaces; the coatings had very small grain-sizes, and showed no orientation relationship with the substrate surfaces.

CONTENTS:

INTRODUCTION

The work described in this thesis is concerned with research into new methods for the electroless deposition of the metals chromium and aluminium from solution onto a dispersed phase, with particular reference to the deposition of these metals directly onto ceramic whiskers for use in the fibre-strengthening of metals; the new methods of metal deposition described are intended to improve upon fabrication methods already in use for the production of fibre-strengthened materials.

Some aspects of fibre-strengthening:

The aim of fibre-strengthening is to improve the strength, creep-resistance, stiffness and toughness of metals and alloys, especially at elevated temperatures; the fibre-strengthening of metals and alloys has been the subject of several recent reviews(1,2) which are of two types: those concerned with reinforcement by continuous fibres, or filaments, and those concerned with reinforcement by discontinuous fibres.

The most successful work on strengthening by continuous fibres is reported to have been in the strengthening of metals such as copper, nickel and chromium with high tensile strength wires of tungsten, molybdenum or stainless steel. These composite materials have been fabricated either by casting the matrix metal around the strengthening wires(3), or by electroplating the wires with the matrix metal(4,5,6).

The best type of discontinuous fibre for strengthening has been found to be the whisker, (7) a single crystal needle, usually of a non-metallic substance, whose diameter is of the order of one micron. It has been shown that, if a whisker is to be effective in strengthening, its length : diameter ratio must be greater than approximately fifty. In whiskers the very low concentration of those crystal imperfections which cause weakness in metals, coupled with the high degree of perfection of the whisker surface, give the whiskers a very high tensile strength along their longitudinal axes, although they are brittle when subjected to stress perpendicular to their longitudinal axes.(8)

A discontinuous fibre-strengthened composite material consists of whiskers, aligned so that their longitudinal axes lie along the axis of greatest tensile strength of the composite, in a metal matrix.(9) The function of the matrix is to bind the fibres together and to protect their surfaces from mechanical damage; the matrix also transfers applied stress to strong fibres, and separates the fibres so that cracks can not propagate entirely in the brittle fibre phase.(8,10) The mechanism of fibre-strengthening is different from that of dispersion hardening, in which the matrix, strengthened by a hard second phase, carries the whole applied load; in a fibre-strengthened material the applied load is carried almost entirely by the fibres, so that the properties of the fibres will govern the properties of a composite material to a very large extent. Strength, toughness, stiffness and resilience are essential properties of whiskers; low density is desirable, so that the strength-weight ratio of a composite material may be made as large as possible.(11)

The efficiency of fibre-strengthening is limited by how well stress can be transmitted between the fibres and the matrix metal (12); this is a function of the bond strength between the fibres and the matrix. The greatest bond strength is attained when a chemical bond joins the surface of the fibres to the matrix(13,14), but to avoid embrittling effects the matrix must not chemically attack the fibres, nor must the fibres dissolve in the matrix. Therefore, for the optimum bond strength an interaction should take place at the fibre-matrix interface, but only to the extent that the fibre and the matrix are brought into intimate contact.(10) The ideal interface consists of the fibre and the matrix in atomic contact, with no intermediate phase formed between them, so that the 'chemical bond' between the two phases is of the very strong short-range van der Waals type. Therefore the nature of the first stage in the fabrication process of a composite material, that is the method by which the matrix metal is brought into contact with the fibres, has a very significant effect on the subsequent properties of the composite.

Conventional Fabrication Methods.

i) Metallurgical methods:

The most commonly used methods reported in the literature include powder metallurgical techniques such as pressing, or hot-pressing, of a compact of metal powder and whiskers, followed by sintering or extrusion, during which bonding between the matrix and the fibres takes place by diffusion. Slip casting followed by sintering has also been used as a fabrication method (10,15). Methods of this type have the disadvantage that bonding between whiskers and matrix metal occurs only when the compact is subjected to stress or high temperature, or both; a whisker is most likely to be mechanically damaged when stress is applied perpendicular to its longitudinal axis, and if bonding occurs by diffusion across the whisker-matrix interface, the sharp interface essential for effective fibre-strengthening is likely to be replaced either by an intermediate phase or by a gradual change from the whisker crystal lattice to that of the matrix metal across the interface.

Direct contacting between the matrix metal in the molten state and the whiskers has been used as a fabrication method, both by liquid metal infiltration of whisker matts, in some cases under vacuum, and by casting a suspension of whiskers in the liquid metal. In certain cases such methods have proved successful in promoting wetting of the whiskers by the matrix, but wetting is probably achieved by a chemical reaction between the two phases, since alumina whiskers have been found to dissolve in molten iron unless they are protected by a coating of a refractory metal such as tungsten.(8) Similarly silicon nitride whiskers have been found to dissolve in molten aluminium.(16) Therefore the danger of mechanical damage to the whiskers and chemical reactions between the whiskers and the matrix make 'metallurgical' fabrication methods undesirable.

ii) Chemical methods:

Solid objects may be plated with metals from the vapour phase, either by physical methods such as evaporation and condensation or sputtering of the metal, or by chemical methods: these include the thermal decomposition of a volatile compound, or the reduction of a volatile compound by hydrogen, a metal vapour, or in some cases by the surface of the solid to be plated.(17) Since there are several vapour phase deposition methods for chromium(17a) and aluminium(17b), the problems encountered during the development of such a process for the fabrication of metal-whisker composites would probably be of a technical, rather than a fundamental chemical, nature. For instance, the whiskers would have to be supported and heated evenly so that an even deposit of metal was formed on them; one possible solution to such a problem would be to carry out a conventional vapour phase deposition process in a fluidised bed of whiskers.

The problem of exposing the whole surface area of a whisker to a deposition process is easily overcome in the liquid phase by maintaining the whiskers in suspension in the liquid. An ideal method of applying an even, overall coating of metal to the whisker at a temperature low enough to prevent diffusional or chemical interaction between the two phases while ensuring good contacting between them is to electroplate the metal onto the whisker. However, ceramic whiskers are not electrically conducting, so that electrodeposition of the matrix metal directly onto the whiskers is not possible. A technique of this type might be developed if the whiskers were first coated with a very thin, firmly bonded layer of an easily deposited metal such as silver, palladium or copper, so that the whiskers became electrically conducting, and if a method of making a matt of whiskers the cathode of an electrolytic deposition process were used, since both chromium and aluminium may be deposited electrolytically, from aqueous solutions in the case of chromium and non-aqueaus solutions in the case of aluminium;(18,19) for instance, the whiskers could be floated on a pool of mercury, which would provide electrical contact with the metal coating on the whiskers, but only if the difficulty of amalgamation could be overcome. However, there would be no direct contact between the whiskers and the electrodeposited metal, so that a method of this type would not constitute a legitimate solution to the problem of forming a direct contact between the whiskers and the matrix metal.

If ceramic whiskers were electrically conducting electrodeposition would constitute an ideal fabrication process, since a metal ion is reduced at the surface of the cathode by electrons supplied by the cathode to form a metal atom which then remains firmly bonded to the cathode surface. Conventional electroless deposition methods are analogous to electrodeposition in that a metal ion is reduced at a surface by electrons, but these electrons are supplied by a chemical reducing agent instead of by an external source; the surface at which the ions are reduced is not cathodic in the normal sense, in that it does not supply electrons directly to the ion, but it must be catalytic to the reduction process.

Conventional Electroless Deposition Methods:

Conventional electroless plating methods are carried out in aqueous solutions, which contain essentially metal ions and a reducing agent, and generally buffering agents and other additives; in many cases the metal ion is complexed. It must be thermodynamically possible for the metal ion to be reduced by both homogeneous and heterogeneous mechanisms; the heterogeneous reduction takes place on specific surfaces in the solution, whereas the homogeneous reduction takes place only in the bulk solution away from surfaces. The presence of a catalytically active surface in the solution increases the rate of the heterogeneous reduction to such an extent that the amount of homogeneous reduction in the solution is negligible in an efficient process, so that all the metal produced by reduction is deposited on the catalytic surface.

Two commonly used reducing agents in electroless deposition are hydrazine and sodium hypophosphite. Hydrazine readily reduces aqueous solutions of divalent palladium compounds to palladium metal(20a) which may be plated onto virtually any solid surface in contact with the solution such as other metals, non-metallic solids including whiskers, the glass vessel in which the reduction is carried out, and even grease on the walls of the vessel. This process has been used to deposit a thin coating of palladium metal onto surfaces which are otherwise inactive in order to render them either catalytically active or electrically conducting.

However, in the electroless plating of nickel by the reduction of divalent nickel compounds in aqueous solution by sodium hypophosphite(21,22) the spontaneous production of nickel metal takes place only on certain catalytically active metal surfaces such as mild steel, cobalt or palladium, but not on other surfaces which are inactive, such as copper, tin, lead or non metals. The heterogeneous reduction may proceed on certain inactive metal surfaces if they are activated by the passage of an electric current for a short time by contacting the metal to be plated with another metal which is lower in the electrochemical series, or 'baser', immersed in the solution. For example, the reduction occurs spontaneously on silver, but not on copper; if, however, the copper specimen to be plated is contacted with a rod of zinc metal immersed in the same solution for several seconds the heterogeneous reduction is initiated and will continue spontaneously after removal of the zinc rod. This contacting renders the copper cathodic and the zinc anodic so that the system acts as an electrolytic cell; the first nickel deposited is in effect electroplated, and subsequently acts as a catalytically active surface for the electroless deposition of nickel when the zinc rod is removed. Certain metals such as zinc, tin and lead can not be coated with nickel by this process even after electrolytic initiation, and non-conducting non-metallic solids can not be activated to the process electrolytically unless they are first coated with a conducting metal layer.

An electroless plating method for chromium:

The process reported in the literature for the electroless deposition of chromium(23) is similar to that described for nickel in that chromic salts are reduced by sodium hypophosphite in aqueous solution. The process is operated at temperatures between 70° and 100°C and at a pH of approximately 4 which is maintained by the buffering action of sodium citrate: the solution contains chromic fluoride, chromic chloride and sodium hypophosphite.

The composition of a simple bath is quoted as

Reagent	gm./gallon of water	gm./litre of water	molality
CrF_3	64	14	0·06
$Cr\ Cl_3$	4	1	0·004
NaH_2PO_2	32	7	0·1

Improved baths contain also acetates and glycollates and nickel salts(24). In the following thermodynamic calculations on this process it is assumed that

i) no appreciable error is introduced by performing the calculations for a temperature of 25°C using data relevant to this temperature.

ii) The metal exists in solution as uncomplexed aqueous Cr^{3+} ions.

iii) The organic species present act only as buffering agents and have no interaction with the chromic ions.

The Pourbaix (E vs. pH)(25) diagrams for the systems phosphorus and water, and chromium and water, have been calculated from data taken from Latimer's 'Oxidation Potentials'(26) (see Appendix 1). In these calculations it was assumed that the activity of each ionic phosphorus species in solution was 10^{-1} molar, and that the activity of each ionic chromium species in solution was 10^{-2} molar: the results are presented in Figure 1.

If it is assumed that the mechanism of the reaction is the reduction of uncomplexed hydrated chromic ions directly to chromium metal by hypophosphite ions which are oxidised to phosphite ions, the reaction may be represented by the equation

$$2\,Cr^{3+} + 3\,H_2PO_2^- + 3H_2O = 3H_2PO_3^- + 6H^+ + 2\,Cr$$

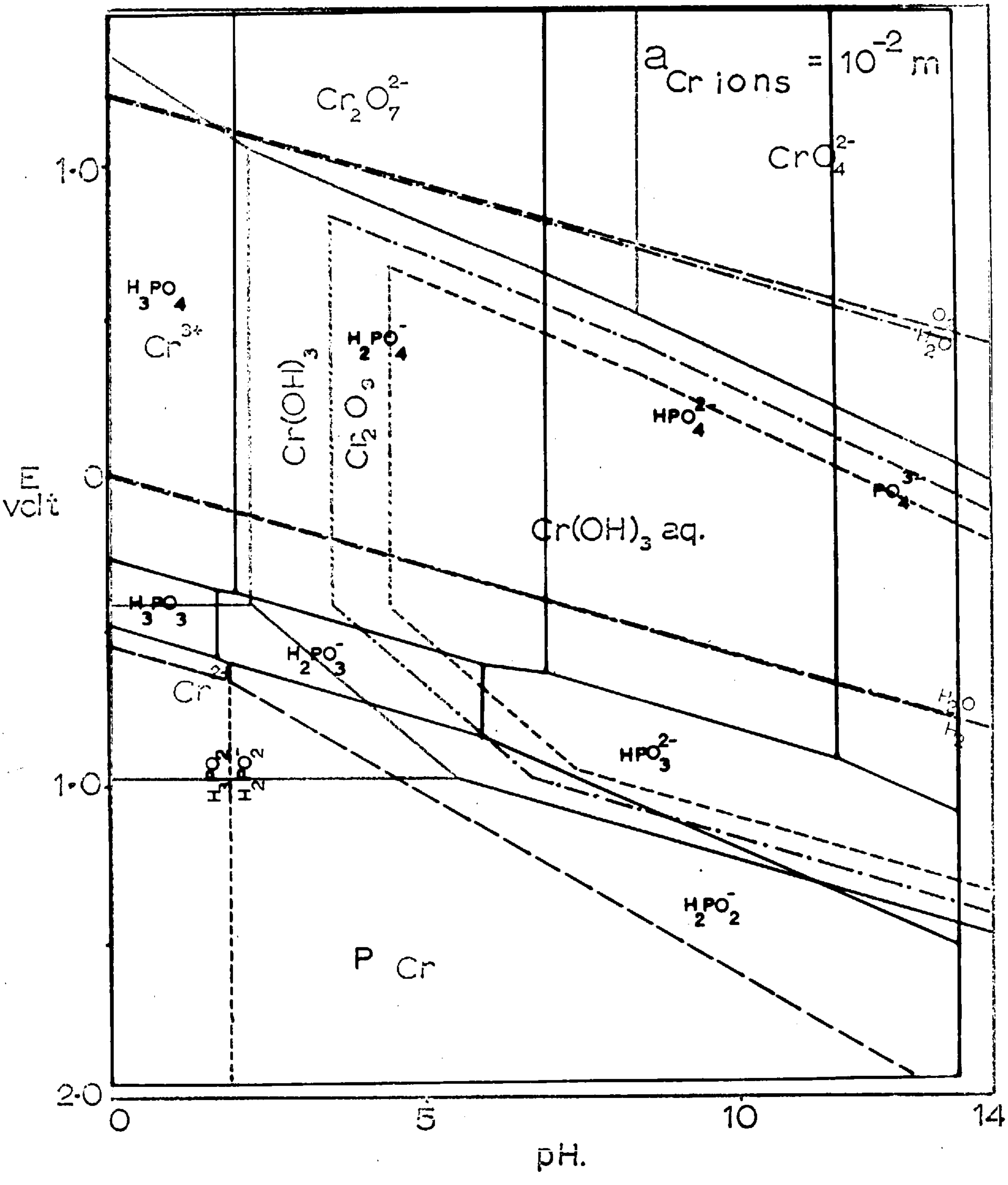
for which $\Delta G^\circ = +\,33{,}250$ cal/mole.

$$\Delta G = \Delta G^\circ + RT\ \ln.\ \frac{(aH_2PO_3^-)^3 \cdot (a\ H^+)^6}{(aH_2PO_2^-)^3 \cdot (a\ Cr^{3+})^2}$$

If pH = 4 and $aCr^{3+} = 10^{-2}$m.

$$\Delta G = +6{,}000 + 4{,}100\ \log.\ \frac{aH_2PO_3^-}{aH_2PO_2^-}$$

so that ΔG is less than zero, allowing the reduction to proceed spontaneously, only when the ratio of the activity of phosphite ion



a Cr ions = 10-2 m
Cr2O7 2-
CrO4 2-
1·0
H3PO4
Cr3+
Cr(OH)3
Cr2O3
H2PO4-
HPO4 2-
O2
H2O
PO4 3-
E
volt
0
Cr(OH)3 aq.
H3PO3
H2PO3-
Cr2+
H3PO2
H2PO2
HPO3 2-
H2O
H2
1·0
H2PO2-
P
Cr
2·0
0
5
10
14
pH.

Fig.1

to the activity of hypophosphite ion is less than $3{\cdot}5 \times 10^{-2}$. Therefore the reduction is thermodynamically possible only if the reducing agent is present in a large excess; since the activity of phosphite is thought to be lowered by the precipitation of chromic phosphite and additions of sodium hypophosphite are made to the bath during the process, the ratio of hypophosphite to phosphite is kept high enough for the reaction to proceed spontaneously.

If similar assumptions are made in the reduction of nickel ions by hypophosphite ions, the reaction may be represented by the equation

$$Ni^{2+} + H_2PO_2^- + H_2O = H_2PO_3^- + 2H^+ + Ni$$

for which $\Delta G^\circ = -21{,}720$ cal/mole.

$$\Delta G = \Delta G^\circ + RT\ \ln.\ \frac{aH_2PO_3^-\ (aH^+)^2}{aH_2PO_2^-\ \ aNi^{2+}}$$

If pH = 4 and $aNi^{2+} = 10^{-2}$ m.

$$\Delta G = -29{,}900 + 1{,}360\ \log.\ \frac{aH_2PO_3^-}{aH_2PO_2^-}$$

so that ΔG is less than zero, allowing the reduction to proceed spontaneously, when the ratio of the activity of phosphite to the activity of hypophosphite is less than 10^{22}. Therefore the reduction is thermodynamically possible even in the presence of a large excess of the oxidised species; as in the case of chromium, the activity of phosphite in solution is lowered by the precipitation of nickel phosphite.

The assumptions made in these calculations are largely invalid, since the elevated operating temperature will have a marked effect on the energy values used, and interaction between cations and anions in solution is appreciable, since the Pourbaix diagram for chromium shows that the chromic ion should be hydrolysed to the insoluble hydroxide at a pH of 4, yet baths of this type are operated using clear solutions. However, even though these calculations are only approximate, they do show that the electroless plating of nickel by this method is considerably thermodynamically more feasible ~~easier~~ than the electroless plating of chromium; nickel plates rapidly, but chromium plates only very slowly under the same conditions. Nickel plates spontaneously onto certain metal surfaces, but chromium begins to plate onto the same metals only after electrolytic initiation.

It has been found that, when nickel and chromium are deposited by hypophosphite reduction, there is invariably some contamination of the metal deposit by phosphorus; this is thought to come from either the metal phosphites precipitated during the deposition process or phosphine liberated during the reduction. The phosphorus content of the deposited metal may be as high as 5 per cent. by weight; phosphorus contamination is most undesirable, because phosphorus has very serious embrittling effects on many metals, and a high concentration in the stress-transferring regions of a metal matrix close to a whisker surface might have very deleterious effects on the properties of a whisker-strengthened composite material.

Since electrolytic initiation is necessary to start the reduction of chromic ions by hypophosphite ions at a surface, this process is not applicable to the formation of a deposit of chromium on a non-conducting solid surface. The nature of the surfaces which are catalytic to the spontaneous deposition of nickel from a hypophosphite bath without electrolytic initiation has not yet been fully elucidated, but generally the nobler the metal and the better abraded its surface, the more readily nickel will deposit spontaneously. All attempts to coat non-metallic surfaces such as matts of whiskers and polycrystalline alumina fibres by this method have been unsuccessful.

Metal deposition by hydrogen reduction:

Many metals, including nickel, may be deposited from aqueous solutions of their ions by reduction with gaseous hydrogen.(27a,28) Nickel is produced by the reduction of a solution of Ni^{2+} ions, complexed with ammonia at a pH of 8, with hydrogen gas under pressure in an autoclave at elevated temperatures. The reaction may be represented approximately by the equation

$$Ni^{2+} + H_2 = Ni + 2H^+$$

At 25°C, $\Delta G^\circ = +11,530$ cal/mole

$$\Delta G = \Delta G^\circ + RT \ln. \frac{(aH^+)^2}{a\,Ni^{2+} \cdot pH_2}$$

If $aNi^{2+} = 10^{-1}$ m. and pH = 8,

then $\Delta G = 0$ when $\log pH_2 = -6\cdot5$

Therefore at room temperature under these conditions the reduction of nickel (11) ions to nickel metal is thermodynamically possible if the pressure of hydrogen applied to the solution is greater than 10^{-6} atmospheres. In practice an operating temperature of 200°C and a hydrogen gas pressure of up to 50 atmospheres are used.

Under similar conditions the reduction of chromic ions in aqueous solution by hydrogen gas may be represented approximately by the equation

$$Cr^{3+} + 1\tfrac{1}{2} H_2 = Cr + 3H^+$$

at 25°C,

$$\Delta G^\circ = +51,500 \text{ cal/mole}$$

$$\Delta G = \Delta G^\circ + RT \ln. \frac{(aH^+)^3}{a\, Cr^{3+} . (pH_2)^{1\frac{1}{2}}}$$

If $a\,Cr^{3+} = 10^{-1}$ m. and pH = 8,

then $\Delta G = 0$ when $\log pH_2 = 15$

Therefore at room temperature under these conditions the reduction of chromic ions to chromium metal is thermodynamically possible only if the pressure of hydrogen applied to the solution is greater than 10^{15} atmospheres, which is far beyond the performance of any pressure vessels currently in use.

Although these calculations are only approximate, and take no account of the elevated temperature normally used, or of the complexing action of ammonia which renders the metal ions soluble to a high pH where they would be hydrolysed to an insoluble hydroxide unless complexed, the calculations do indicate that, while nickel ions may be readily reduced to nickel metal by hydrogen gas, the reduction of chromic ions to chromium metal by the same process is practically impossible.

It has been found that nickel metal may be plated onto small ceramic fibres by the hydrogen reduction of solutions of nickel (11) ions only after the fibres have been activated to the process by the previous application of a thin coating of a suitable metal such as palladium.

The Pourbaix diagram for the aluminium-water system has been calculated : Figure 2 and Appendix 1. Al^{3+} ions are even more difficult to reduce to aluminium metal from aqueous solutions than the equivalent chromium ions ; aluminium can be electroplated only from non-aqueous solutions, for example by the electrolysis of aluminium halides or hydrides in anhydrous organic solvents.

Aqueous elctroless plating methods such as those described previously are not applicable to the formation of a coating of chromium or aluminium on non-metallic fibres because of the large reducing potentials required and the need to activate the fibres by the application of a thin active metal coating. In the experimental section which follows, unsuccessful attempts to extend conventional aqueous electroless plating methods to non-aqueous solutions are described, followed by the successful solution of the problem by the thermal decomposition of organic solutions of organometallic compounds of chromium and aluminium.

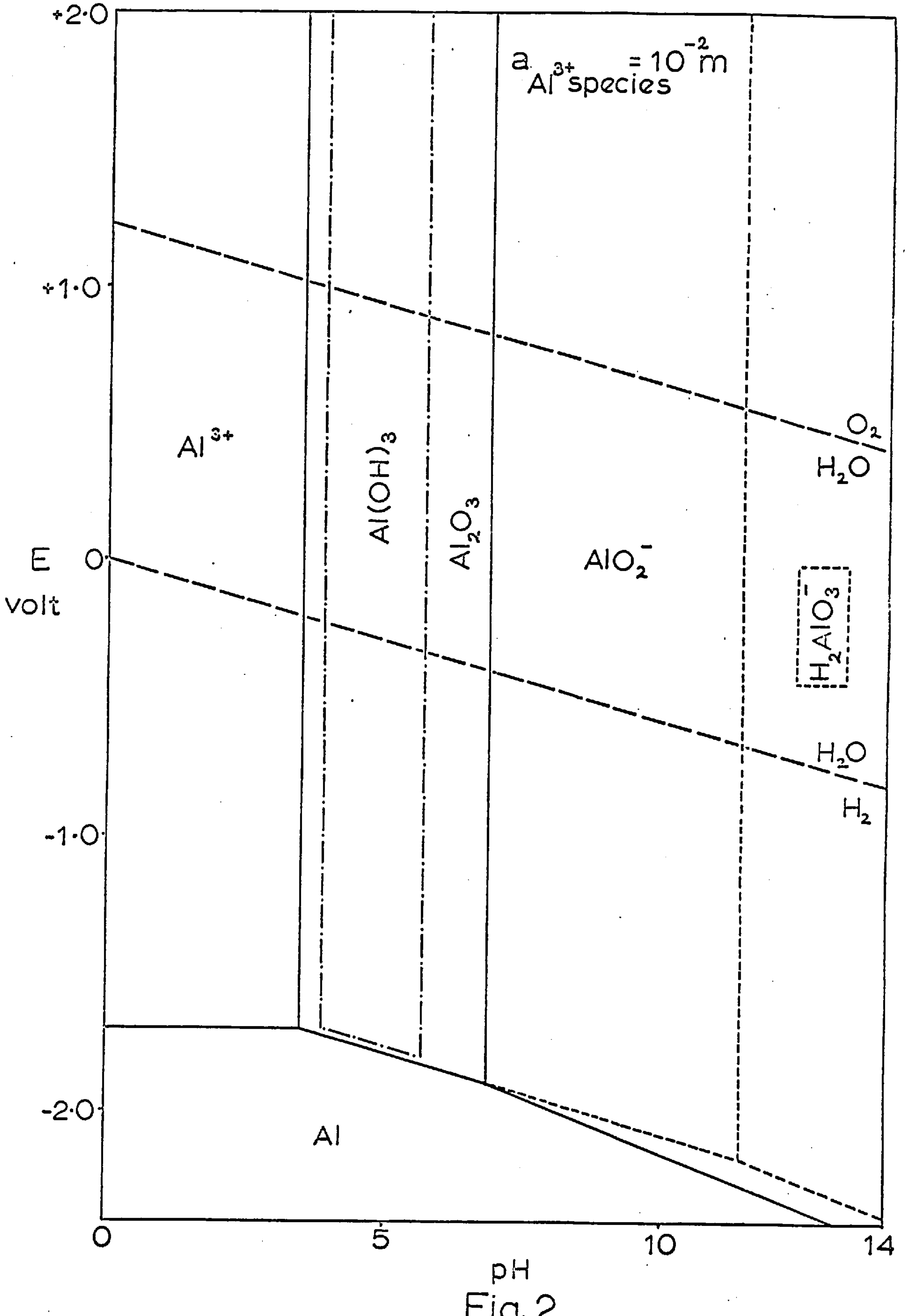

+2·0
+1·0
0
-1·0
-2·0
E
volt
$a_{Al^{3+} species} = 10^{-2}$ m
Al^{3+}
$Al(OH)_3$
Al_2O_3
AlO_2^-
$H_2AlO_3^-$
O_2
H_2O
H_2O
H_2
Al
0
5
10
14
pH

Fig. 2.

EXPERIMENTAL

Introductory:

Types of non-metallic fibres studied in metal deposition experiments:

Three types of ceramic fibre were studied during investigations into the ability of various systems to deposit chromium or aluminium from solution, namely polycrystalline alumina rods, silicon carbide whiskers and silicon nitride whiskers.

The polycrystalline alumina fibres, which had been fabricated by sintering techniques, were not detectably porous although they were of a very small grain size: their sides were macroscopically smooth, but microscopically rough because of their granular nature. The average diameter of the fibres was in the region of 0·5 mm., and they were generally used in lengths of 2 cm. during deposition studies. The fibres were easily cleaned by soaking in concentrated nitric acid, washing with distilled water and drying with acetone; although the fibres were fairly brittle, they were easy to handle, and their bright white crystalline appearance under microscopic examination made the detection of any metal deposited on them very easy.

The silicon carbide, SiC, whiskers had a grey-green appearance en masse; microscopic examination showed that there was a large variation in the shape, size and appearance of the whiskers, from short, thick whiskers with fairly jagged edges to long, fine whiskers with very smooth edges. The average length and diameter of the whiskers was determined by sprinkling a small sample onto a microscopic grid with 10 micron spacings and estimating the dimensions of each whisker in the field of view under microscopic examination. It was found that the silicon carbide whiskers had an average diameter of (3 ± 1) microns and an average length of (50 ± 25) microns. Taking the density of silicon carbide as 3·22 gm./cc. it was calculated that the surface area per gram of whiskers was 4×10^3 $cm.^2/gm.$

The silicon nitride, Si_3N_4, whiskers had a dull white appearance en masse; microscopic examination showed that there was little variation in the size, shape and surface appearance in the whiskers, which were mostly long and fine with very smooth faces. The average dimensions of the whiskers was determined as for the silicon carbide whiskers, and it was found that the silicon nitride whiskers had an average diameter of ($1 \cdot 3 \pm 0 \cdot 6$) microns and an average length of (100 ± 50) microns. Taking the density of silicon nitride as 3·44 gm./ cc. the surface area per gram of silicon nitride whiskers was calculated to be 9×10^3 $cm.^2/ gm.$

Potentially useful deposition methods were first examined for their ability to deposit metal onto polycrystalline alumina fibres; these were selected because of their ease of handling and detection of deposited metal, and because this type of alumina is cheaper and more readily obtainable than whiskers. It was assumed that any system incapable of depositing metal onto polycrystalline alumina would also be incapable of depositing metal onto single-crystal whiskers under the same conditions. Processes which gave a satisfactory metal deposit on polycrystalline alumina were examined further for their ability to plate metal onto other solid surfaces; the results of such investigations will be described in the section dealing with successful plating methods.

Chemical reduction in non-aqueous solvents:

Several unsuccessful attempts were made to extend conventional aqueous electroless deposition methods to chemical reduction in non-aqueous solvents, including liquid ammonia and various ethers: these non-aqueous solvents have the advantage that very strong reducing agents such as the alkali metals or lithium aluminium hydride may be used without reduction of the solvent.

Reduction of chromic halides in liquid ammonia: (29,30)

Chromic chloride, bromide and iodide are soluble in anhydrous liquid ammonia to form strongly solvated chromic species in solution. The metals sodium and potassium are soluble in anhydrous liquid ammonia, and act as strong reducing agents:

$$E^\circ \ K^+/K = -2{\cdot}73 \text{ volt.} \qquad E^\circ \ Na^+/Na = -2{\cdot}59 \text{ volt.}$$

However the activity of sodium or potassium in solution is lowered by side reactions such as the formation of amides;

$$Na + NH_3 = Na\,NH_2 + \tfrac{1}{2} H_2.$$

Anhydrous chromic chloride and chromic iodide were prepared by the direct combination of the metal and the halogen in the absence of air in both cases; anhydrous liquid ammonia was obtained by boiling off ammonia gas from a concentrated aqueous solution, drying the gas by passing it through quicklime towers, and condensing the gas in a vessel cooled in a mixture of solid carbon dioxide and acetone.

Both chromic halides were soluble in liquid ammonia, with the formation of an orange-pink solution. Sodium and potassium metals were soluble in liquid ammonia with the formation of a deep blue solution. Reduction of the chromic compounds to chromium metal by the alkali metals was not achieved, even when the reducing metal was present in a large excess, although some colour change was seen when the two solutions were mixed.

It is reported in the literature that the iodides of the metals gold, silver, copper, nickel and manganese may be reduced with sodium or potassium in liquid ammonia to the metals in a finely divided and very reactive state. However, no reduction of chromic iodide in liquid ammonia has been reported.

Reduction of chromic chloride in ether solution by sodium naphthalide:

Chromic chloride is soluble in tetrahydrofuran (THF), and may be reduced with sodium naphthalide in the presence of tetramethylethane-diphosphine in solution to form a zerovalent complex of chromium of formula $Cr(Me2\ PC_2\ H_4\ PMe2)3$.(31,32)

The reduction of anhydrous chromic chloride in THF solution by sodium naphthalide in the absence of any phosphorus-containing ligand was attempted; sodium naphthalide was prepared by heating sodium metal and naphthalene together in THF under reflux in a nitrogen atmosphere until a yellow-green solution was obtained. This solution, containing sodium naphthalide, was decanted from the unreacted sodium and added to a solution of chromic chloride in THF; this was then heated for several hours under reflux in a nitrogen atmosphere, but no metallic chromium was found to have formed, either as powder by homogeneous reduction, or deposited on the polycrystalline alumina fibres immersed in the solution.

The thermal decomposition of the zerovalent complex of chromium quoted above to give chromium metal might be possible, but would be undesirable as an electroless plating method because of the danger of phosphorus contamination of any metal produced.

Reduction of chromic chloride by lithium aluminium hydride:

The attempted reduction of THF solutions of chromic chloride by lithium aluminium hydride yielded ambiguous results; a deposit was formed after mixing chromic chloride solution and lithium aluminium hydride solution. The deposit was shown to contain both chromium and aluminium, but its precise chemical nature was not established.

These unsuccessful attempts to extend conventional electroless plating methods to non-aqueous solvents were not explored in any further detail. As a general principle a spontaneous heterogeneous deposition of a metal onto an inactive surface occurs only when the reduction of the metal from solution is very easy, as in the case of the reduction of palladium (II) ions by hydrazine in aqueous solution; as the reduction becomes more difficult, the activation of the surfaces on which the metal is to be deposited becomes more necessary. Since both chromium and aluminium are difficult to reduce from any solution, the activation of non-metallic surfaces to be coated with either metal would presumably be essential in any system dependent on reduction of oxidised metal species in solution by a chemical reducing agent. The added disadvantage of possible chemical contamination of any metal produced by the reducing agent, or its decomposition products, makes such methods inapplicable to the formation of a firmly adherent layer of either chromium or aluminium directly on a non-metallic surface.

Thermal Decomposition of Zerovalent Metal Compounds:

Successful electroless deposition methods described in the following sections are based on the thermal decomposition of compounds in which the formal oxidation state of the metal is zero. In a conventional electroless process metal is produced by direct reduction of the metal in an oxidised state by a reducing agent : the principle of the new methods described later is as follows:

i) An oxidised species of the metal is reduced to an oxidation state of zero in the presence of certain complexing agents which remain bonded to the zerovalent metal, to form a zerovalent compound.

ii) The zerovalent compound is isolated and, if necessary, purified.

iii) A solution of the zerovalent compound, containing a suspension of the solid to be coated with metal, is heated to a temperature at which the zerovalent compound decomposes to liberate the ligand and form metal at the solid surfaces by a heterogeneous mechanism

Desirable properties of zerovalent compounds used in processes of this type are as follows:

1) The compound must be easy to obtain or prepare, easy to handle and store, and reasonably inexpensive.

2) The decomposition temperature of the compound must not be prohibitively high.

3) The compound must have a low vapour pressure at the decomposition temperature so that it does not tend to sublime out of solution.

4) The ligand molecules liberated from the compound on thermal decomposition must be chemically stable at the decomposition temperature in the presence of the finely divided metal produced.

5) The ligand molecules liberated must be capable of rapid removal from the site of the heterogeneous reaction, preferably in the form of a gas, or as a species soluble in the solvent used for the process.

Compounds in which chromium exhibits a formal valency of zero and which are thermally decomposable to form chromium metal were restricted, where possible, to those with stable organic ligands without reactive functional groups. The compounds investigated were

i) The "sandwich" compound bis-benzene-chromium (0), $Cr(C_6H_6)_2$.

ii) Tris - 2,2' bipyridyl chromium (0)

iii) Chromium hexacarbonyl

iv) Chromium arene tricarbonyl compounds, (Arene) $Cr(CO)_3$.

Desirable properties of solvents for zerovalent compounds are as follows:

1) The solvent must form a true solution with the compound, not just a fine suspension of the compound.

2) The solvent must be liquid at the decomposition temperature of the compound ; the decomposition temperature must be below the boiling point of the solution, since boiling encourages homogeneous nucleation in the solution.

3) The temperature range over which the solvent is liquid should be as large as possible.

4) The solvent should have a low vapour pressure at the decomposition temperature.

5) The solvent must not undergo any chemical reaction with the zerovalent compound or any of its decomposition products, and must be stable in the presence of any reactive, finely divided metal produced.

Therefore the solvents used in this work have been restricted, where possible, to paraffin hydrocarbons or stable, preferably fully conjugated, unsaturated hydrocarbons.

Further requirements of an electroless plating method are that it should be relatively simple to perform and should be easily developed from small, laboratory scale experiments to a method capable of handling large volumes of fibres. Most of the work described in the following sections was carried out with volumes of solution in the region of 10 ml.

SECTION 1 : CHROMIUM.

THERMAL DECOMPOSITION OF BIS-BENZENE CHROMIUM.

Bis-benzene chromium (o), $Cr(C_6H_6)_2$, exists as brown-black crystals which melt under nitrogen at 285°C and undergo rapid thermal decomposition at 300°C; at room temperature it is appreciably soluble only in benzene and its homologues. It oxidises readily in air to form derivatives of the $Cr(C_6H_6)_2^+$ cation; these are soluble in water, but not in non-polar organic solvents.

Bis-benzene chromium is isoelectronic with Ferrocene and, like Ferrocene, is a "sandwich" bonded compound: its structure has been established and discussed elsewhere.(33,34) The main features of the compound's structure relevant to this work are:

i) The central chromium atom is symmetrically bonded to two eclipsed, planar, undistorted benzene rings.

ii) There is no formal carbon-metal bond in the compound: bonding is formed by overlap of the delocalised π-orbitals of the benzene rings and the orbitals of the metal atom.

iii) With respect to electrons involved in bonding, the compound is isoelectronic with Krypton, and so has an 'inert gas configuration'.

iv) The chromium atom is in an oxidation state of zero in the compound; the dipole moment of the compound has been found to be zero, and the compound is diamagnetic.

v) The standard heat of formation of the compound from chromium and benzene in the solid phase is

$\Delta H_f \quad (C_6H_6)_2 Cr, c \quad = \quad 35 \pm 15$ kcal/mole

and in the gas phase is

$\Delta H_f \quad (C_6H_6)_2 Cr, g \quad = \quad 53{\cdot}7 \pm 15$ kcal/mole.(35a)

The thermal decomposition of bis-benzene chromium (o) in a suitable solvent has the advantage that the only products of the decomposition are chromium metal and benzene, which is a stable gas at 300°C and so would be rapidly removed from the decomposition site by evolution from the solution.

Bis-benzene-chromium (o) may most conveniently be prepared by a two stage process (36,37): the first stage consists of the preparation of the bisbenzenechromium (1) cation by the reduction of anhydrous chromic chloride by aluminium metal in the presence of benzene and anhydrous aluminium chloride, which acts as a Friedel-Crafts catalyst:

$$3\,CrCl_3 + 2\,Al + AlCl_3 + 6\,C_6H_6 = 3\left[Cr(C_6H_6)_2\right]^+\left[AlCl_4\right]^-$$

The second stage consists of the reduction of this cation by alkaline aqueous sodium dithionite to the zerovalent compound, and the extraction and purification of this compound.

Anhydrous chromic chloride was prepared by heating powder chromium metal in a stream of chlorine and collecting the sublimed violet solid. Aluminium metal powder was washed thoroughly with benzene. Aluminium chloride lump, GPR grade, was ground to a fine powder in air and loaded as quickly as possible to avoid hydrolysis. Analar benzene was used as supplied.

The bisbenzenechromium (1) cation may be prepared by two methods: on a small scale the reactants are heated in a sealed tube which is rotated at 150°C ; on a larger scale the reactants are heated under reflux in an inert atmosphere. During the first stages of this work the cation was prepared by heating 5 gm. anhydrous chromic chloride, 0·7 gm. aluminium powder, 12 gm. anhydrous aluminium chloride and approximately 50 ml. benzene in an evacuated and sealed thick-walled glass tube. The tube was packed in a brass pipe which was rotated inside a tube furnace at 100 r.p.m. for twelve hours at 150°C.

The second method was found to be more satisfactory for preparation on a larger scale, and in larger yield; 25 gm. anhydrous chromic chloride, 3·5 gm. aluminium powder, 60 gm. anhydrous aluminium chloride, 100 ml. benzene and 0·3 ml. mesitylene, as a catalyst, were heated under reflux in a dry, oxygen-free nitrogen atmosphere for 36 hours, with stirring.

The reaction product from both methods was transferred to a flask containing a vigorously stirred mixture of benzene, methanol and an aqueous solution of potassium hydroxide and sodium dithionite under nitrogen. Unreacted aluminium chloride was hydrolysed, and the water-soluble bisbenzenechromium (1) cation was reduced to the benzene-soluble zerovalent compound, which was extracted into the benzene layer. The reduction was complete after two hours, when the aqueous layer became almost colourless and the benzene layer a very dark brown.

Solutions of the zerovalent compound were handled as far as possible under a stream of nitrogen to prevent oxidation. The benzene layer was sucked into separating funnels, separated from any aqueous matter which settled, and dried over potassium hydroxide pellets. The benzene was then distilled off under vacuum to leave a solid residue of the zerovalent compound, which was washed with air-free diethyl ether to remove organic impurities, and then sublimed under vacuum. The purified product was stored under nitrogen: its yield was generally in the region of 50% of the theoretical yield. A more detailed description of the experimental procedure may be found in Inorganic Syntheses. Vol.6, p.132.

Preliminary Experiments:

0.25 gm. of solid bisbenzenechromium was heated in a glass tube under nitrogen; the melting of the black crystals was followed by the rapid formation of a silvery metal mirror on the inside of the glass tube.

It was assumed that the decomposition temperature of a solution of the zerovalent compound would not be appreciably higher than that of the solid compound, so that the boiling point of any solvent should be above 300°C.

Although at room temperature the compound is soluble only in benzene and its homologues such as toluene, xylene, etc. it was thought that it might be soluble in a solvent not of benzenoid character at elevated temperatures; the use of the straight-chain paraffin hydrocarbon, normal Octadecane, $CH_3(CH_2)_{16}CH_3$, as a solvent was therefore investigated. The advantage of this paraffin was that it could be obtained in a pure form and had well-characterised melting and boiling points of 29°C and 307°C; the melting point of 29°C meant that it could be handled easily as either a solid or a liquid.

0·5 gm. bisbenzenechromium and 10 gm. n-Octadecane were heated together in a flask under nitrogen; at 200°C the black solid dispersed in the colourless liquid paraffin, and the liquid had a homogeneous black appearance at 250°C. The liquid was heated at 305°C for 15 minutes, and then allowed to cool to room temperature, when the contents of the flask were washed out with acetone and filtered; the black solid residue was insoluble in hot organic solvents and mineral acids, and was identified as chromium metal powder of undetermined purity by X-Ray fluorescence and X-Ray powder diffraction methods.

The thermal decomposition of 0·5 gm. bisbenzenechromium in 10 gm. nOctadecane at 305°C was repeated with several polycrystalline alumina fibres immersed in the liquid; black chromium powder was again produced, but no metal was deposited on the alumina fibres. The concentration of the compound was increased to 1·0 gm. and then 2·0 gm. in 10 gm. nOctadecane but no deposition of metal on the fibres was found.

Turbotherm A, a commercial heat-transfer liquid, is a colourless liquid hydrocarbon with a low vapour pressure and a boiling point of 390°C; it is specified as "an isomeric mixture of triaryldimethanes". All attempts to use it as a solvent for the thermal decomposition of bisbenzenechromium to give a deposit of chromium metal on polycrystalline fibres failed, resulting in the production of chromium metal powder only.

Aromatic hydrocarbons with boiling points greater than 300°C and strongly benzenoid characteristics generally have high melting points, above 200°C; the suitability of these as solvents was therefore investigated by using equal weight mixtures of the high boiling-point aromatic hydrocarbons with nOctadecane, with which they are miscible at all temperatures. It was expected that bisbenzenechromium would be soluble in fully conjugated aromatic hydrocarbons, but Anthracene (which is not fully conjugated), Phenanthrene and para-diphenyl-benzene mixtures with n-Octadecane as solvents gave only chromium powder on thermal decomposition of bisbenzenechromium solutions, and were undesirable because they sublimed when heated.

Trans - 1,2 - diphenyl ethylene (t - Stilbene) and 1, 4, diphenyl-buta 1, 3, diene are fully conjugated, and have a phenyl group substituted at both ends of an olefin, ethylene and conjugated butadiene respectively. When a solution of bisbenzenechromium in an equal weight mixture of n-Octadecane and t -Stilbene was heated to 305°C under nitrogen, an even coating of chromium metal was deposited on several polycrystalline alumina fibres immersed in the solution; t -Stilbene melts at

124°C and boils at 307°C, and is miscible with n-Octadecane in all proportions. A similar result was achieved by replacing t - Stilbene by 1,4 diphenyl buta 1,3 diene in this process, but since t-Stilbene is much cheaper and more readily obtainable, a more detailed study of the thermal decomposition of solutions of bisbenzenechromium in t-Stilbene and n-Octadecane only was made.

Apparatus:

Experiments on the thermal decomposition of solutions of bisbenzenechromium were carried out in 250 ml. round-bottomed flasks under dry, air-free nitrogen or argon ; the flask was heated in a fluidised sand both whose temperature could be controlled to within ± 1° at 300°C. The temperature of a hydrocarbon liquid inside the flask was measured in terms of the temperature of the fluidised bath to avoid the necessity of immersing a thermometer in the plating solution, since an effective electroless plating method would deposit metal on the thermometer; between 300° and 320° the temperature of the contents of the flask was found to be between 5° and 6° below that of the fluidised bath. A rubber balloon was included in the inert atmosphere system so that after evacuation and filling of the system at room temperature, expansion of the insert gas during heating was taken up by the balloon, which acted as a reservoir. A diagram of the apparatus is shown in Fig.3.

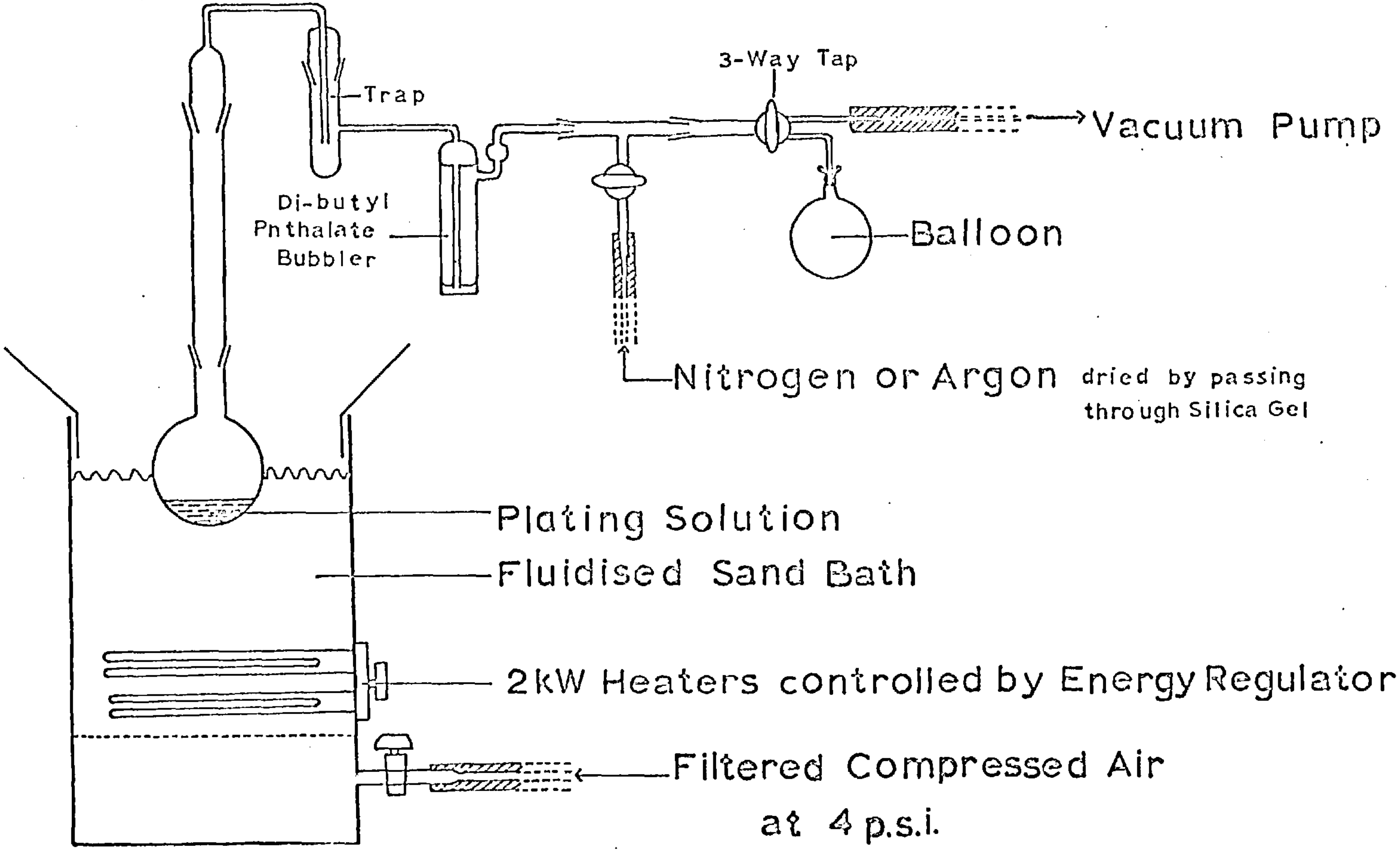

3-Way Tap
Trap
Vacuum Pump
Di-butyl Pnthalate Bubbler
Balloon
Nitrogen or Argon dried by passing through Silica Gel
Plating Solution
Fluidised Sand Bath
2kW Heaters controlled by Energy Regulator
Filtered Compressed Air at 4 p.s.i.

Fig. 3.

Effect of Solvent:

Solutions consisting of a total weight of 10gm. solvent and 0·5 gm. bisbenzenenechromium were thermally decomposed to produce a deposit of chromium metal on polycrystalline alumina fibres ; the ratio of normal Octadecane to trans-Stilbene in the solvent was varied, with the following results:

i) Pure n-Octadecane gave no plated metal from such a system.

ii) A mixture of 2gm. t-Stilbene and 8gm. n-Octadecane gave an uneven, patchy coating of chromium metal.

iii) A mixture of 5gm. t-Stilbene and 5gm. n-Octadecane gave an even metal coating on the polycrystalline alumina fibres.

iv) Pure t-Stilbene gave an even plate of chromium metal on polycrystalline alumina fibres, but sublimation of both solute and solvent gave appreciable decomposition on the walls of the flask above the solution.

The equal weight mixture of n-Octadecane and t-Stilbene was therefore adopted as a suitable solvent, since it had a wide range of temperature over which it was liquid (30°C to 307°C), a low vapour pressure and little tendency to sublime.

Effect of Concentration:

Solutions consisting of 5gm. t-Stilbene and 5gm. n-Octadecane and different weights of bisbenzenechromium were thermally decomposed to give a deposit of chromium on polycrystalline fibres. It was found that as the concentration was increased, a limiting thickness of metal deposited on the fibres was reached.

The amount of chromium deposited from a solution of 2gm. bisbenzenechromium in 10gm. solvent was found to be not appreciably greater than that from a solution containing 1gm. of the compound in 10gm. solvent, although sublimation, deposition on the flask walls and the homogeneous production of metal powder increased. At concentrations below 0·5 gm. bisbenzenechromium in 10gm. solvent the metal coating on the fibres was patchy, and an insoluble green residue was formed; this residue was similar in characteristics to the atmospheric oxidation product of the zerovalent compound.

A concentration of between 0·5gm. and 1·0gm. bisbenzenechromium in 10gm. solvent was therefore adopted as a suitable solution composition for this method.

Effect of Temperature and Time:

The precise temperature at which the decomposition of the solution begins has not been determined; however, a heating bath temperature of 308°C, which gave a solution temperature of 302°C, caused complete thermal decomposition within five minutes, while a heating bath temperature of 300°C, which gave a solution temperature of 295°C, caused no decomposition of the solution. Since the decomposition of the solid at 300°C is rapid, it is reasonable to assume that it is equally as fast in solution, so that the rate of the decomposition can not be controlled by variations in temperature in this type of system. Chromium deposited on polycrystalline alumina fibres from a solution which was heated to 310°C was no different from that deposited from a solution heated to 302°C.

Effect of Stirring:

Mechanical stirring was found to have an undesirable effect on the plating properties of the system; it appeared to encourage the homogeneous production of chromium metal powder at the expense of the chromium deposited on the alumina fibres. Volatilisation of both solute and solvent and metal deposition on the flask walls above the solution were increased on stirring, as was the amount of the solid green oxidised side-product. The green solid was insoluble in benzene, but soluble in hot dilute mineral acids; on ignition it burned reluctantly with a smoky flame to leave a green solid residue, which infers that the solid is either a compound containing an oxidised cation of bisbenzenechromium or chromic oxide contaminated with hydrocarbon solvent.

Effect of substrate:

The ability of the method to deposit chromium onto the following surfaces was investigated:

activated alumina, polycrystalline alumina, palladium coated polycrystalline alumina, polished gold, a single crystal sapphire, glass, silicon nitride whiskers.

In each case a solution of 1gm. bisbenzenechromium in 5gm. t-Stilbene, 5gm. n-Octadecane was heated under argon at 303°C for fifteen minutes to ensure complete decomposition of the solution. The system was allowed to cool to room temperature, and the contents of the flask were washed out with hot chloroform and filtered; the solid residue was washed several times with hot solvents to remove organic impurities and then dried. In all cases except the silicon nitride whiskers, chromium metal powder produced by homogeneous decomposition could be wiped from the solid surface to leave the adherent metal deposit.

a) Activated Alumina:

Chromatographic alumina in lump form was activated at 300°C ; about 0·5gm. was immersed in the deposition bath. After the decomposition reaction it was found that the alumina was heavily coated with metal, and the amount of metal powder produced by homogeneous decomposition was appreciably reduced. No oxidised by-product was found.

b) Polycrystalline Alumina Fibres:

Several fibres immersed in the solution were completely coated with chromium metal; the good 'Throwing Power' of the method was shown by the fact that the ends of the fibres were coated to the same extent as their sides, and small holes and recesses in the fibres could be seen to be coated.

c) Palladium coated alumina fibres:

Polycrystalline alumina fibres were coated with a thin layer of palladium metal by the thermal decomposition of an acetone solution of chloropalladic acid.(20b) 0·5gm. $PdCl_2$ was dissolved in 10ml. hot stirred concentrated hydrochloric acid through which chlorine was bubbled until a clear solution was obtained. This solution was then cooled, and diluted to 50ml. in acetone. Alumina fibres were dipped in this solution and then held in a blast of hot air from an air dryer; the solution evaporated, and the solid residue decomposed at about 300°C to give an even coating of palladium metal; this process was repeated several times, until a visible metal coating was produced. Complete decomposition was ensured by subsequently heating the fibres in an oven at 300°C for an hour. This method gave a more even metal coating than the method of dipping followed by simple static drying in the oven.

The thin palladium coating on the alumina fibres had no apparent effect on the deposition of chromium; fibres coated along half their lengths with palladium, the other half being bare alumina, were evenly coated with chromium along their whole lengths. No difference in thickness or nature of the chromium deposit was detectable between the two ends of the fibre.

d) Gold Metal:

A rectangular block of gold, 1cm. square and 3mm. thick, was polished and buffed to a smooth, shiny finish, and immediately immersed in the plating solution to give a metallic, oxide-free surface in contact with the solution. Thermal decomposition of the solution gave a thin, even coating of chromium metal on the gold; the coating was blue-black and metallic in appearance.

e) Single Crystal Sapphire:

A single crystal of sapphire, gamma alumina, in the form of a disc of diameter approximately 1cm. and thickness 2mm., with the flat faces polished to optical flatness but the circumference rough ground with a small 45° bevel, was immersed in the solution together with a polycrystalline alumina fibre. After thermal decomposition the alumina fibre was well coated with chromium; the rough-ground circumference and bevel were evenly coated with black chromium metal, but the flat faces were more thinly coated with grey, translucent chromium. This coating was thickest at the periphery, and became progressively thinner towards the centre, disappearing at 2mm. from the edge.

This result indicates that on any given solid the deposition of chromium proceeds more readily on a rough rather than a smooth surface, and infers that in this case the deposition of chromium is nucleated at the rough edge and grows in towards the centre of the smooth face.

f) Glass:

The 250ml. round-bottomed flask which contained the solution during each decomposition reaction became coated with chromium metal over the area with which the solution was in contact; this coating was fairly even in each case, with extensive patches of mirror metal formed.

g) Silicon Nitride whiskers:

0·1gm. silicon nitride whiskers was dispersed in the solvent, in one case by stirring the whiskers into a very viscous oil which was then mixed with the solution, and in another case by stirring the whiskers directly into the solvent which had been liquified by warming.

Microscopic examination revealed that about 60% of the whiskers had chromium metal deposited on them after thermal decomposition of the solution; whiskers were generally either not coated at all or completely coated. The coatings had a nodular, uneven appearance, but there was no indication that the coating was thicker at the ends of the whiskers than at the smooth centre sections.

Rotating Disc Experiments:

The reaction by which chromium metal is deposited on a solid surface is heterogeneous in character; the homogeneous production of chromium metal powder in solution is in effect an undesirable side-reaction. Heterogeneous reactions may be partly or wholly controlled by transport of solute through solution to the surface at which the heterogeneous reaction takes place; such reactions may be studied by rotating disc experiments which have been comprehensively reviewed elsewhere.(27b,38)

Polycrystalline recrystallised alumina cylindrical crucibles were mounted for use as rotating discs by setting a nut in Plaster of Paris inside the cylinder, as shown in Fig.4. This technique was also used for mounting glass cylinders with

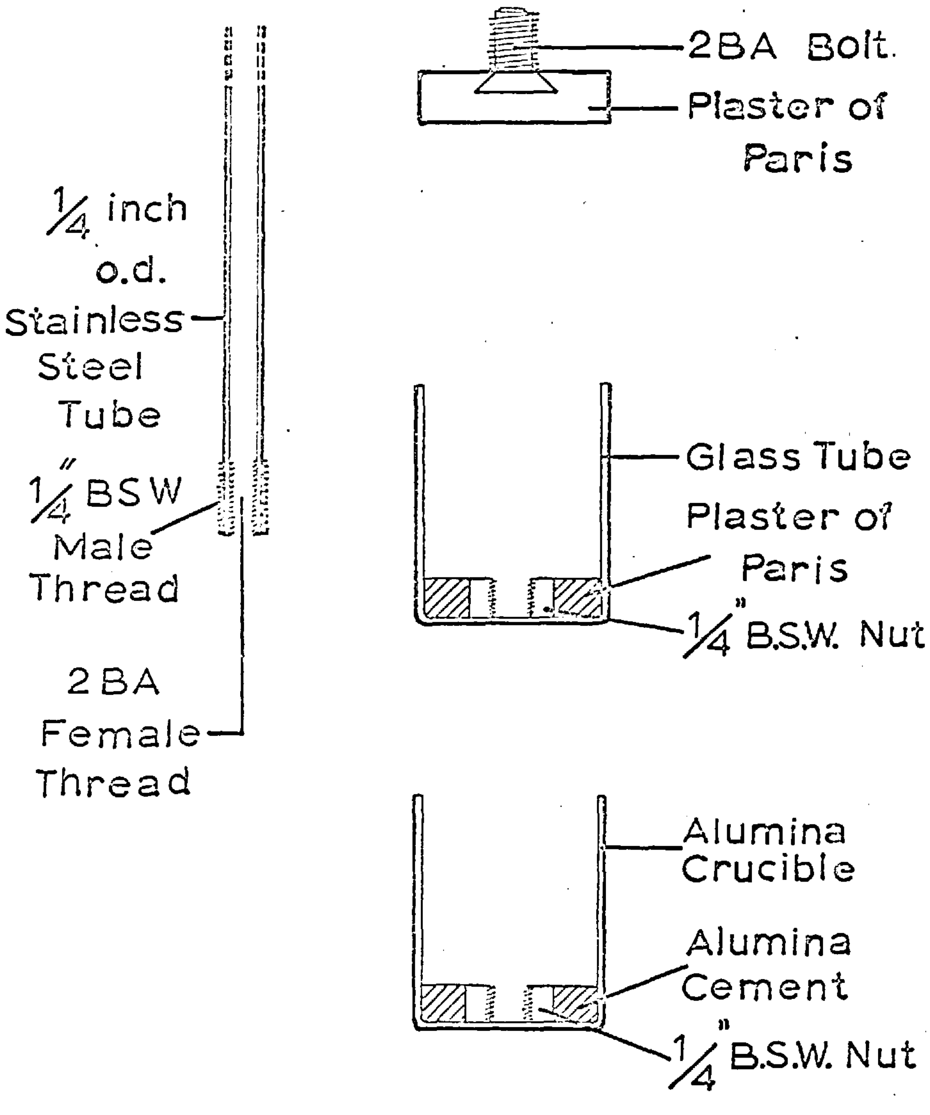

1/4 inch o.d. Stainless Steel Tube
1/4" BSW Male Thread
2BA Female Thread
2BA Bolt.
Plaster of Paris
Glass Tube
Plaster of Paris
1/4" B.S.W. Nut
Alumina Crucible
Alumina Cement
1/4" B.S.W. Nut

Fig. 4.

closed, flat-ground ends. An aluminium cylinder was anodised at 25 volts to give a layer of hydrated alumina some 300Å thick; this was then baked at 300°C to dehydrate the alumina. A Plaster of Paris disc was also prepared by setting a bolt in Plaster of Paris in a disc-shaped mould, and turning the resulting approximate shape down on a lathe to a smooth, flat disc concentric with the bolt.

The conditions of the ideal rotating disc experiment were reproduced as nearly as possible by rotating the cylinders at the minimum depth of immersion; speeds of rotation of 100 r.p.m. and 500 r.p.m. were used. The 250ml. flask shown in the apparatus in Fig.3 was replaced by the reaction vessel shown in Fig.5 ; the rotating shaft was kept gas-tight by the use of a PTFE 'stuffing box' lubricated with silicone oil.

Deposition of chromium onto the cylinders was attempted by rotating them at small depths of immersion in solutions of 3gm. bisbenzenechromium in 15gm. t-Stilbene and 15gm. n-Octadecane: no deposition of chromium on the alumina or glass surfaces was achieved under these conditions. Because of the failure of the first two attempts, a polycrystalline alumina fibre was immersed in the solution; this was found to be coated with chromium metal, as from a static bath, even when no chromium was found to be deposited on the rotating cylinders immersed in the solution after thermal decomposition. The stirring action of the rotating cylinder increased volatilisation of the solution, and

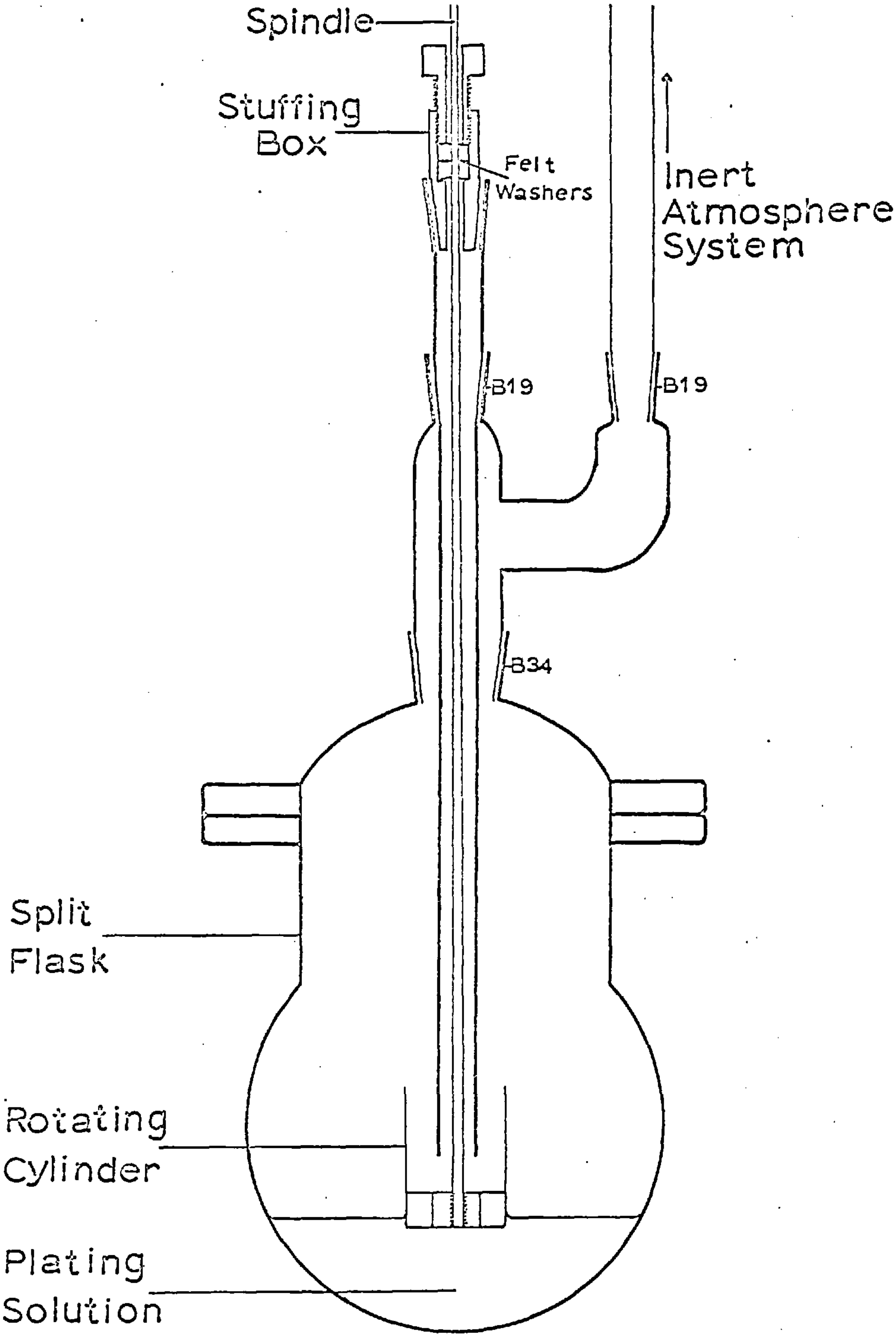

Spindle
Stuffing Box
Felt Washers
Inert Atmosphere System
B19
B19
B34
Split Flask
Rotating Cylinder
Plating Solution

Fig. 5.

although no metal was deposited on the rotating surface from solution, an appreciable amount of metal was deposited from the vapour phase above the solution, accompanied by some oxidised product, on both the flask walls and the sides of the rotating cylinder. (Plate 1).

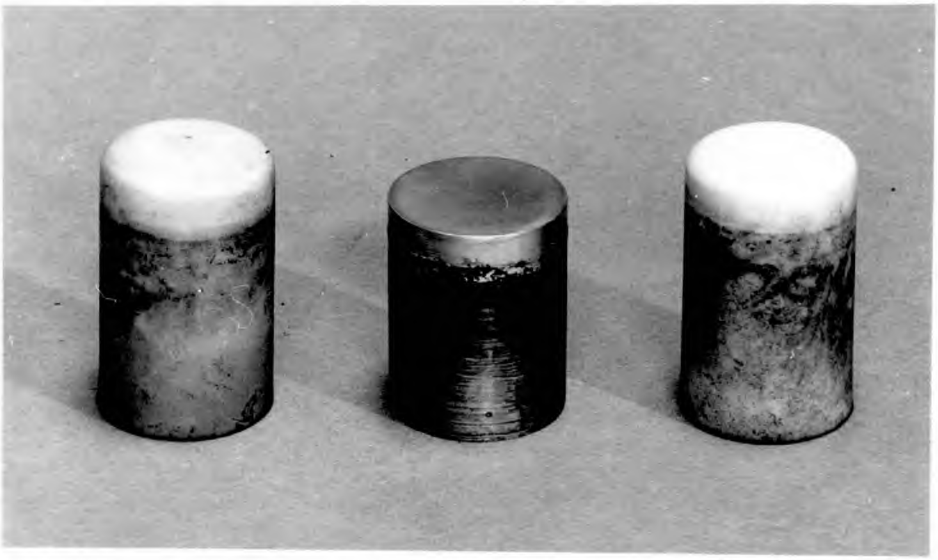
The thermal decomposition of a solution of the same composition in the presence of a rotating disc of Plaster of Paris resulted in the deposition of black chromium metal on all the exposed outer surfaces of the disc; the deposited metal extended 2mm. into the bulk of the disc from each surface. Because this disc was very porous, it was probable that the disc had soaked up a volume of the solution before the decomposition temperature had been reached, so that the decomposition did not take place at the surface of the disc but in the bulk of the solid.

The failure of the thermal decomposition of the solution to deposit metals onto rotating discs of alumina indicated that this method could not be used to study the kinetics of the decomposition reaction. The failure infers either that

i) The reaction is so sensitive to temperature that, even under the conditions of stirring caused by the rotating cylinder, it occurs preferentially near the heated walls of the reaction vessel and not evenly throughout the solution, or

ii) stirring encourages homogeneous metal powder formation at the expense of heterogeneous metal deposition.

Plate I



(i) (ii) (iii)

(i) Polycrystalline Alumina crucible rotated at 100 rpm.

(ii) Anodised Aluminium cylinder rotated at 100 rpm.

(iii) Polycrystalline Alumina crucible rotated at 500 rpm.

showing the failure of the thermal decomposition of bisbenzenechromium solutions to deposit chromium on rotating discs of alumina immersed in solution, although some is deposited from the vapour above solution.

Since a fibre at the bottom of the solution was coated with chromium even when the rotating surface was not, the former explanation was thought to be more likely. No further attempts to investigate the kinetics of this method of metal deposition were made.

Effect of Impurities:

The presence of any oxidation product of bisbenzenechromium in the solution was found to have a very deleterious effect on the ability of the bath to deposit chromium metal on a solid surface. Any visible oxidation of the black crystals of the zerovalent compound, shown by a green appearance, caused the chromium metal deposit formed on alumina fibres by thermal decomposition of a solution to be thin and patchy.

Effect of Metal Compound:

Bisbenzenechromium is the simplest of the sandwich-bonded zerovalent chromium compounds; homologous compounds may be prepared by the same method as that described previously by replacing benzene by its appropriate homologue.

Since the ring to metal bond is formed by the overlap of metal atom orbitals and the delocalised π-orbital of the benzene ring, it is reasonable to assume that the strength of this bonding will be affected by the Inductive effect of substituents in the benzene ring. Substituents which tend to withdraw electrons from the delocalised orbital, such as chlorine, should weaken the bonding and so lower the decomposition temperature; those which tend to push electrons into the delocalised π- orbital, such as methyl groups, should strengthen the bonding and raise the decomposition temperature, if it is assumed that the Inductive effect acts alone. The only thermodynamic data available are the mean bond dissociation energies for Cr - benzene, (40·5 ± 8) kcal/mole ; Cr-mesitylene, (41·5±2) kcal/mole ; Cr - cumene, (41.0 ± 2) kcal/mole.(35b) Within the limits of the errors quoted, no significant trend is shown by these values.

No synthesis of bischlorobenzene chromium (0) has been reported in the literature; attempts to prepare the bischlorobenzenechromium by the reduction of anhydrous chromic chloride by aluminium in the presence of anhydrous aluminium chloride and chlorobenzene resulted in the production of a dark brown tarry compound which left no solid residue on ignition.

The synthesis of the cations bistoluenechromium (1) and bismesitylenechromium (1) by the same method was in both cases accompanied by heavy tarring, which is not unusual in reactions which proceed by a Friedel-Crafts mechanism. Shaking the product of this reaction with active charcoal or actuated alumina was not found to be an efficient method of removing the tar, since most of the cationic compound was removed at the same time. The tar was allowed to remain during reduction to the zerovalent compound and removal of the solvent by vacuum distillation; the solid residue was then washed with ether saturated with nitrogen prior to purification of the zerovalent compound by vacuum sublimation, but the resulting yield of the compound was very low.

Apart from the extra difficulties encountered during their preparation, another immediately apparent disadvantage of the zerovalent toluene and mesitylene homologues of bisbenzenechromium was their increased sensitivity to atmospheric oxidation; on one occasion a freshly purified sample of bistoluenechromium(0) ignited spontaneously on contact with air. Solutions of these conpounds at high temperatures were subject to increased volatilisation, which was accompanied by vapour deposition of metal and oxidised by-product on the walls of the flask above solution, compared with solutions of the benzene homologous compound. Only patchy deposits of chromium were produced on polycrystalline alumina from the thermal decomposition of solutions of bistoluenechromium and bismesitylenechromium in equal weight mixtures of t-Stilbene and n-Octadecane heated to 305°C.

Similar difficulties were encountered in the synthesis of bisbenzene molybdenum (0), a small sample of which was prepared by the reaction of $Mo\ Cl_5$ with aluminium, aluminium chloride and benzene, under the same conditions described previously; the zerovalent molybdenum compound was found to be extremely air sensitive, and no deposit of molybdenum metal was produced on polycrystalline alumina by the thermal decomposition of bisbenzenemolybdenum in solution in trans-Stilbene and normal Octadecane.

Recovery of Solvent:

Once the standard solvent for the thermal decomposition of bisbenzenechromium had been established as an equal weight mixture of trans-Stilbene and normal-Octadecane, the residue from each solution used was collected with the purpose of purifying and recovering the solvent. After removal of the chromium plated articles, the contents of the flask after each thermal decomposition generally consisted of finely divided chromium metal powder, oxidised side-products and the hydrocarbon solvent mixture; the contents of the flask were washed out with hot chloroform, which dissolved the hydrocarbons. The liquid was filtered until clear and colourless, then the chloroform was distilled off, with vacuum applied towards the end of the distillation, to leave the hydrocarbon mixture as a liquid which solidified at room temperature.

When the solvent from about fifteen runs had been recovered, it was seen to have a faint yellow colour: this was at first thought to be due to either unreacted bisbenzenechromium or a decomposition product of one or both hydrocarbons. A 2gm. sample was ignited in a porcelain crucible, and left a very small solid green residue which was soluble in dilute hydrochloric acid, and was assumed to be chromic oxide. The yellow colouration was worked up by fractional recrystallisation from ethanol until about 5c.c. of a solution having a fairly strong yellow colour was obtained; this solution still contained appreciable amounts of the hydrocarbons. The solution was evaporated to dryness, and a small amount of the solid was dissolved in benzene and left in contact with a 5 molar aqueous potassium hydroxide solution in air, with occasional shaking. A small sample of bisbenzenechromium was dissolved in benzene and left in contact with a 5 molar potassium hydroxide solution in air, under the same conditions. Within a day the bisbenzenechromium (0) solution had oxidised completely to leave a colourless benzene layer and a green-coloured aqueous layer; however, the yellow benzene solution of solvent residue remained unchanged, showing no sign of oxidation or dissolution in the alkaline aqueous layer.

These tests indicate that the yellow colouration is due to one or more organometallic compounds which are not bisbenzenechromium, but were formed by an interaction between the zerovalent compound and trans-Stilbene in the solution. The Infra-Red and Ultra-Violet spectra of the concentrated yellow substance were compared with the spectra of the initial solvent; no new peaks were found, and the predominant spectrum in each case was that of trans-Stilbene.

Direct preparation of the yellow compound was attempted by heating 1.5gm. bisbenzenechromium and 1gm. t-Stilbene together under nitrogen for several hours at 260°C, then to 305°C to decompose unreacted bisbenzenechromium. The contents of the flask were dissolved in hot chloroform, which was filtered and evaporated: the recovered t-Stilbene again had a yellow colour, but spectroscopic examination revealed no new peaks in the t-Stilbene spectrum.

Chromatographic separation of a cyclohexane solution of the yellow compound on activated alumina indicated that there were two distinct yellow compounds, both of which were strongly absorbed on the alumina.

The exact nature and composition of the yellow compounds have not been determined, since they were not fully isolated from the hydrocarbon solvents. However, their occurrence indicates that bisbenzenechromium is soluble in t-Stilbene because of some interaction between them at high temperatures, but the extent of compound formation is too small to impair the plating efficiency of the method.

Nature of Metal Deposit:

In all cases the metal coating produced by the method described in this section was electrically conducting, but insoluble in mineral acids, even after extensive washing of the specimens with organic solvents to remove any film of organic material, followed by boiling the specimens in the acid for several days.

The purity of the chromium metal deposited was found to be not less than 98 per cent. (see "Analytical Methods" section).

The main impurity in the chromium was carbon; electron-probe microanalysis has shown that carbon is present up to about 2 per cent. and is evenly distributed. A vapour phase deposition method for chromium based on the thermal decomposition of bis-cumenechromium gives chromium metal with a carbon content of up to 15 per cent. by weight.

An even chromium metal deposit of thickness between 1 and 5 microns has been produced by this method; the chromium has been found to adhere very firmly to all surfaces on which it has been deposited. The deposit on the highly polished faces of the single crystal sapphire disc could be removed only by polishing it off; this was also found to be the only way of removing the chromium deposit from the gold block. The hardness and ductility of the metal deposit have not been established, because of the thinness of the deposit.

No evidence was found of any crystal growth in the chromium deposit, or of any crystallographic relationship between the deposit and the substrate surface. A Laué back-reflection X-Ray diffraction pattern of the single crystal sapphire disc, with the optically flat faces normal to the X-Ray beam, was taken before the disc was coated with metal. The clear pattern of spots obtained confirmed that the disc was a single crystal, and rotation of the stereographic projection of the crystal obtained showed that the optically polished faces of the disc were high index planes: one (100) type plane was parallel to the face, and the two others were inclined at 3^{o} to the polished face.

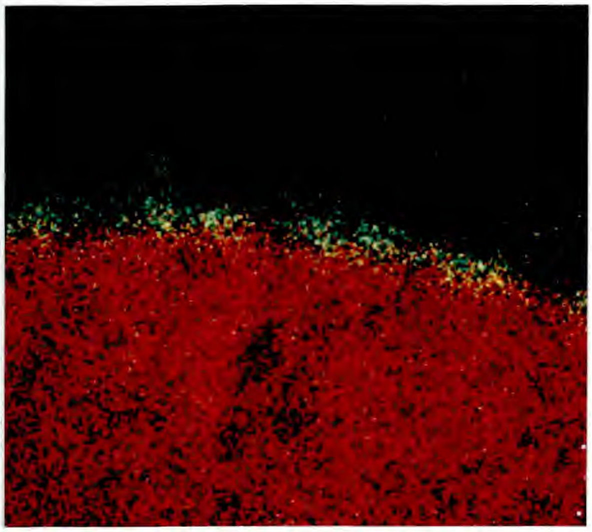
Lauė photographs taken under the same conditions of the chromium coated sapphire disc were fogged, and showed no characteristic pattern for chromium, which indicated that either the chromium deposit was too thin to be detected by this method, or the grain size of the metal was very small: the fogging of the film inferred the latter. Any large crystal growth in the chromium deposit would have been shown by the appearance of additional series of spots on the Lauė photographs.

Low angle of incidence electron diffraction studies of the chromium deposit on the sapphire disc and the gold block indicated that the chromium had a very small grain size.

The cross-section of several chromium coated alumina fibres was examined by setting the fibres in mounting resin and polishing : the specimen was scanned by the electron-probe microanalyser for aluminium and chromium, and the results are shown in Plates 2, 3 and 4. The aluminium scan was displayed on a screen with a red filter and photographed; the chromium was then displayed on the same screen behind a green filter, and photographed on the same exposure. The line scan for aluminium, chromium and the surface profile was also displayed and photographed. These results show that the chromium deposit is in close contact with the alumina surface.

Electron Probe Microanalysis.

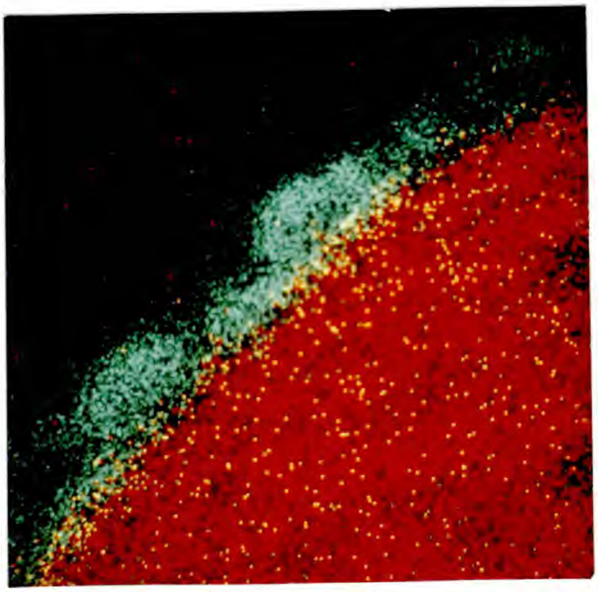
Plate 2



Green Trace = Chromium
Red Trace = Aluminium
in Alumina.

Plate 3

Green Trace = Chromium
Red Trace = Aluminium
in Alumina.



Electron Probe Microanalysis.

Plate 4

Green Trace = Chromium

Red Trace = Aluminium

in Alumina.

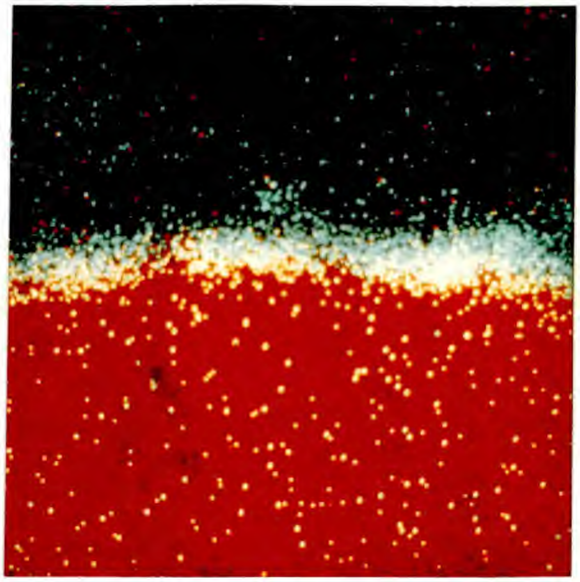
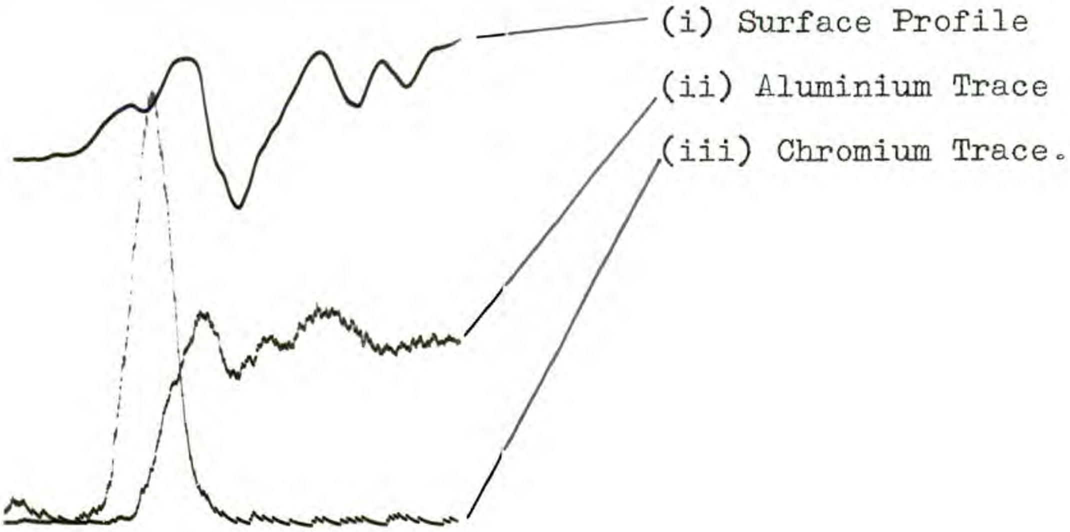


Plate 5



Discussion:

The thermal decomposition of a 10 per cent by weight solution of zerovalent bisbenzenechromium in an equal weight mixture of trans-Stilbene and normal-Octadecane under an inert atmosphere will deposit a thin layer of reasonably pure chromium metal on both metallic and non-metallic solid surfaces immersed in the solution.

The main disadvantages of the method are the lengthy preparation of the zerovalent compound, or its high cost if purchased, and the necessity for storing it under dry, oxygen free conditions because of its sensitivity to atmospheric oxidation. The decomposition reaction seems to be practically uncontrollable because of its fast rate once the decomposition temperature has been reached; this may explain why a limiting thickness of deposit is reached when the concentration of the zerovalent compound in the solution is increased. If the homogeneous and heterogeneous reactions both proceed at approximately the same very fast rate, and only the compound in the immediate vicinity of the solid surface decomposes by a heterogeneous mechanism, the rest of the compound in solution will have decomposed by a homogeneous mechanism to form metal powder before it can travel through the solution to the heterogeneous reaction site. Therefore the most effective way to operate such a process is to suspend the greatest possible amount of solid to be plated in the solution, so that decomposition leads to the formation of a thin metal deposit over a large area in a short time, rather than to immerse a small amount of solid to be plated and to try to control the homogeneous reaction so that a thick metal deposit is built up over a relatively small area. The method is therefore suitable for the application of a thin deposit of chromium metal to whiskers, but not for the building up of a thick deposit of chromium on a large solid object.

SECTION 2 : CHROMIUM.

Chromium hexacarbonyl:

Chromium hexacarbonyl, $Cr\ (CO)_6$, is readily obtainable commercially as white, air stable crystals; it is isoelectronic with nickel tetracarbonyl, $Ni\ (CO)_4$.

The standard heat of formation of $Ni\ (CO)_4$ is

- (150·4 ± 1·5) k cal/mole in the liquid phase

and - (143·8 ± 1.5) k cal/mole in the gas phase,(35c)

and the mean bond dissociation energy for nickel-carbonyl is (35·2 ± 0·5) kcal/mole.(35b) The reaction

$$Ni + 4CO = Ni\ (CO)_4$$

is reversible at temperatures up to 200°C. Nickel tetracarbonyl may be prepared by direct combination of nickel and carbon monoxide; it may be thermally decomposed in the gas phase up to 200°C to give a deposit of very pure nickel metal.(17c) At higher temperatures carbon is deposited along with nickel.

The standard heat of formation of $Cr\ (CO)_6$ is

- (257·6 ± 0·6) k cal/mole in the solid phase

and - (240·4 ± 1·0) k cal/mole in the gas phase.(35d)

and the mean bond dissociation energy for chromium-carbonyl is (29·5 ± 0·3) k cal/mole.(35b) However, none of the sixth group transition metals form carbonyls by direct reaction between the metal and carbon monoxide, and the reaction

$$Cr + 6\ CO = Cr\ (CO)_6.$$

is not reversible: chromium hexacarbonyl is prepared either in low yield by modified Grignard reactions, or most conveniently by the action of carbon monoxide under pressure on a suspension of chromic chloride, aluminium and aluminium chloride in benzene in an autoclave:

$$\mathrm{Cr\,Cl_3 + Al + 6CO \xrightarrow[Al\,Cl_3]{C_6\,H_6} Cr\,(CO)_6 + Al\,Cl_3}$$

The attempted gas phase thermal decomposition of chromium hexacarbonyl at temperatures of 450°C and above is reported to have led to the deposition of chromium metal very heavily contaminated with chromic oxide and chromium carbide.(17)

In some preliminary experiments on the thermal decomposition of solutions of chromium hexacarbonyl in unreactive hydrocarbon solvents, in which the hexacarbonyl is very soluble, decomposition was found to begin at relatively low temperatures between 120° and 200°C to give a faint mirror deposit on the walls of the flask in which the solution was heated; however, the chromium hexacarbonyl tended to sublime out of solution very heavily.

A solution of 0·5 gm. $Cr(CO)_6$ in 5gm. n-Octadecane was heated to 200°C in a nitrogen atmosphere; sublimed chromium hexacarbonyl was periodically returned to the solution mechanically. The solution decomposed, but no deposit of chromium metal was found on polycrystalline fibres immersed in the solution; the green solid residue from this decomposition was soluble in dilute hydrochloric acid, and consisted mainly of chromic oxide.

Similar results were found after the thermal decomposition of chromium hexacarbonyl in other unreactive solvents; in no case was metallic chromium produced by either homogeneous or heterogeneous reactions.

2,2' - Bipyridyl - chromium compounds:

2,2' - bipyridyl forms zerovalent complexes with many metals; tris - 2,2' - bipyridyl chromium (0), Cr $(bipy)_3^0$ may be prepared by the reduction of a solution of anhydrous chromic chloride in tetrahydrofuran (THF) in the presence of 2,2'-bipyridyl with lithium bipyridyl according to the reactions

$$CrCl_3 + 3\ bipy \xrightarrow{THF} Cr(bipy)_3^{3+}.\ 3\ Cl^-.$$

$$Li + bipy \xrightarrow{THF} Li(bipy).$$

$$Cr(bipy)_3^{3+}.\ 3\ Cl^- + 3\ Li(bipy) \longrightarrow Cr(bipy)_3^0 + 3\ LiCl + 3\ bipy.$$

The zerovalent complex is reported to decompose to chromium metal and bipyridyl when it is heated under vacuum.(39)

The zerovalent complex was prepared in a glove-box with a dry argon atmosphere by the method described above. Approximately stoichiometric quantities of chromic chloride and bipyridyl were dissolved in THF to form a cloudy pink suspension of the chromic complex. Lithium metal was shaken with a solution of bipyridyl in THF until a red solution of lithium bipyridyl was formed. An excess of the lithium bipyridyl solution was added to the solution of the chromic complex, which was sealed under argon and shaken mechanically for several hours until black crystals of $Cr(bipy)_3^0$ separated. However, the zerovalent compound was found to be extremely air sensitive, and difficult to isolate and purify.

A more simple and straightforward method of preparing the zerovalent compound is to heat chromium hexacarbonyl with an excess of 2,2' - bipyridyl in an inert solvent under reflux in an inert atmosphere: a convenient solvent is decalin.(40) The reaction occurs in two stages:

$$Cr(CO)_6 + bipy \xrightarrow{Decalin} Cr(CO)_4\,bipy + 2CO$$

$$Cr(CO)_4\,bipy + 2\,bipy \longrightarrow Cr(bipy)_3 + 4\,CO$$

During this preparation $Cr(CO)_4$ bipy separated as deep red air stable crystals; $Cr(bipy)_3$ formed a black solution, which was very air sensitive.

Because of the sensitivity of the zerovalent compound to atmospheric oxidation, any process dependent on the isolation and purification of the compound, before the preparation of a solution whose thermal decomposition would lead to the deposition of chromium metal, would be undesirable. The thermal decomposition of bipyridyl derivatives of chromium hexacarbonyl will be discussed in the next section, which describes the development of a single stage process for the decomposition of chromium hexacarbonyl derivatives.

THERMAL DECOMPOSITION OF ARENE CHROMIUM TRICARBONYL COMPOUNDS.

Three of the six carbonyl groups in chromium hexacarbonyl may be replaced by a benzenoid aryl compound with a delocalised π - orbital to form an arene chromium tricarbonyl compound(41,55) according to the equation

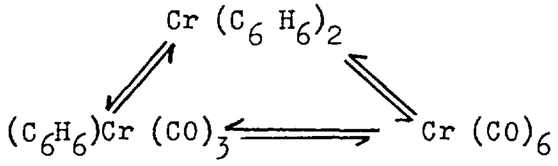
$$\text{Arene} + Cr(CO)_6 \longrightarrow (\text{Arene})\,Cr(CO)_3 + 3\,CO$$

The compound undergoes thermal decomposition to the arene, carbon monoxide and chromium:

$$(\text{Arene})\,Cr(CO)_3 \longrightarrow \text{Arene} + Cr + 3\,CO.$$

In many cases the arene may contain substituted functional groups which survive the conditions of the preparative reaction, but in this work the arenes used have been restricted to hydrocarbons, with the exception of chlorobenzene.

The reactions



are reversible. Benzene chromium tricarbonyl may be prepared by:

i) The reaction between bisbenzenechromium and chromium hexacarbonyl at a high temperature;(42)

ii) The action of carbon monoxide under pressure on bisbenzenechromium;(43)

iii) The reaction between chromium hexacarbonyl and benzene at a high temperature.(43,44)

Since chromium hexacarbonyl is readily obtainable, the direct reaction between $Cr(CO)_6$ and the arene is the simplest method of preparing the arene chromium tricarbonyl compound. The reaction may be carried out in two ways: if the arene is a liquid of boiling temperature higher than 120°C, an excess of the arene may be used as a solvent; if the arene is a liquid of low boiling point, or a solid, an inert solvent such as decahydronaphthalene (decalin), b.pt. 195°C, or diethylene-glycol dimethyl ether (diglyme), b.pt. 163°C must be used. Chromium hexacarbonyl and arene chromium tricarbonyl compounds are soluble in organic solvents; since the compounds formed have appreciable dipole moments, diglyme is thought to be the better solvent since its character is more polar than decalin, but the higher boiling point of decalin made it a more useful solvent for this work.

Arene chromium tricarbonyl compounds were prepared in fairly large yield by the reaction between chromium hexacarbonyl and

Chlorobenzene	b.pt.	130°C
Benzene	b.pt	90°C
Toluene	b.pt	110°C
Mesitylene	b.pt	165°C

both by heating the carbonyl and the arene together under reflux in a nitrogen atmosphere, and by heating a solution of the carbonyl and the arene in decalin or diglyme in a nitrogen atmosphere: for the benzene and toluene compounds the latter procedure only was successful. In all cases chromium hexacarbonyl sublimed heavily from solution, to which it was periodically returned with a metal rod, at temperatures above 100°C: this method was found to be just as effective as, and far simpler than, the method of washing sublimed carbonyl back with refluxing solvent.(45)

The arene chromium tricarbonyl compounds were isolated as yellow-orange crystals contaminated with unreacted chromium hexacarbonyl. When heated under nitrogen, solutions of these compounds in decalin underwent thermal decomposition at approximately the following temperatures:

Chlorobenzene $Cr(CO)_3$	125°C
Benzene $Cr(CO)_3$	160°C
Toluene $Cr(CO)_3$	195°C (boiling solvent)
Mesitylene $Cr(CO)_3$	Solvent boiled before decomposition.

This trend in decomposition temperature indicates that the Inductive effect of the substituent in the benzene ring has an effect on the strength of the ring-metal bond in the compound: chlorine tends to withdraw electrons from the delocalised π-orbital and weaken the bond, whereas methyl groups tend to push electrons into the benzene ring, strengthening the bond. The Inductive effect alone, however, does not explain the higher decomposition temperatures encountered in compounds formed by arenes of higher molecular weight, described later.

The possibility of preparing the arene chromium tricarbonyl compound and decomposing it to chromium metal powder in the same solution was investigated. Chlorobenzene chromium tricarbonyl was found to be difficult to prepare in large yield, because once formed it quickly decomposed at temperatures above about 120°C. 2gm. chromium hexacarbonyl heated in 15ml. chlorobenzene boiling under reflux for five hours gave black chromium metal powder in almost quantitative yield. Similarly, 3gm. $Cr(CO)_6$ heated in 10 ml. decalin, 10 ml. chlorobenzene at 140°C gave black chromium metal. However, these thermal decompositions gave no deposit of chromium metal on polycrystalline alumina fibres or silicon nitride whiskers immersed in the solution.

At low concentrations, below about ·5gm. $Cr(CO)_6$ in 20 ml. solvent, no black chromium metal powder was formed, but a powdery green solid appeared in suspension in the liquid. This solid was insoluble in organic solvents, but reluctantly soluble in hot 5N hydrochloric acid, and so was assumed to be either an oxidised species of the compound, or chromic oxide heavily contaminated with organic matter.

At higher concentrations, up to 5 gm. $Cr(CO)_6$ in 20 ml. solvent, some black chromium was deposited on the wall of the flask at the surface of the liquid, along with metal powder formed by homogeneous decomposition in solution; the chromium deposited on the glass did not form a mirror, and was easily removed from the glass by scraping. Even at the highest concentration no chromium was deposited on any solid immersed in the solution.

The black chromium metal powder produced by homogeneous thermal decomposition in solution was washed extensively with hot chloroform and acetone to remove organic impurities; it was found to be soluble in hot dilute sulphuric acid with difficulty. The solution was made alkaline with sodium hydroxide and boiled with hydrogen peroxide to oxidise the green chromic ions to yellow chromate ions; the solution was then acidified with sulphuric acid to dichromate. 25.00 ml. 0.IN ferrous sulphate solution was added by pipette, and excess ferrous sulphate was titrated against 0·I N potassium dichromate solution. By this method the purity of the chromium was found to be generally in the region of 95 per cent., but in many cases it was not possible to dissolve the whole sample.

Similar results were obtained from the thermal decomposition of benzene, toluene and mesitylene chromium tricarbonyls in solution in decalin and Turbotherm A at several concentrations; at low concentrations a powdery green oxidation product was formed, and at higher concentrations chromium powder was produced homogeneously, but no metal deposit was formed on polycrystalline alumina fibres, with or without a palladium coating, or on silicon nitride whiskers immersed in the solution.

The failure of these methods led to the investigation of the thermal decomposition of arene chromium tricarbonyl compounds formed between chromium hexacarbonyl and arene hydrocarbons of higher molecular weight in inert solvents of high boiling point; the solvents used were normal Octadecane $CH_3(CH_2)_{16}CH_3$,, b.pt. 307°C, normal Eicosane, $CH_3(CH_2)_{18}CH_3$, b.pt 343°C, and normal Docosane, $CH_3(CH_2)_{20}CH_3$, b.pt. 327°C.

The arene hydrocarbons investigated were: Naphthalene, Tetrahydronaphthalene (Tetralin), Anthracene, Phenanthrene, Biphenyl, para - and meta - diphenyl benzene (p-Terphenyl and m-Terphenyl), trans 1,2 diphenyl ethylene (t-Stilbene) and 1,4 diphenyl - buta 1,3 diene. 2,2' bipyridyl was also investigated, although it does not form an arene chromium tricarbonyl compound in the same way as an arene hydrocarbon.

Preliminary experiments on the thermal decomposition of solutions of chromium hexacarbonyl in mixtures of several of the arenes listed above and n-Octadecane indicated that such systems might be effective in depositing chromium metal onto the surfaces of solid objects immersed in solution. To determine the relative effectiveness of the various arenes in these systems, a series of semi-quantitative experiments was carried out in the following way:

1 gm. chromium hexacarbonyl was mixed with 5 gm. of the appropriate arene hydrocarbon and 5 gm. paraffin hydrocarbon, and five polycrystalline alumina fibres were suspended in the

mixture, in a 250 ml. round-bottomed flask with a removable lid; this was then transferred to the argon atmosphere glove-box and heated slowly in a mantle. The contents of the flask had generally formed a clear solution by 150°C; the solution was heated at 200°C for an hour, until a substantial amount of the yellow-orange arene chromium tricarbonyl compound was seen to have formed. Subliming chromium hexacarbonyl was returned to the solution by a glass rod. The temperature of the solution was then raised until a black deposit began to form, and was kept constant at 5°C above this temperature until the decomposition appeared to be complete; this time was in the region of five minutes. The flask was then cooled to room temperature, when the alumina fibres were removed, washed, dried, and examined microscopically for deposited chromium.

Tetralin, Naphthalene, Anthracene and Phenanthrene solutions gave poor, patchy deposits which appeared to be heavily contaminated with a green oxidised by-product: Biphenyl solutions gave no detectable deposit at all. Terphenyl solutions gave thin, dark, patchy deposits which appeared to be oxide free. t-Stilbene and diphenyl-butadiene solutions gave thick, dark, even deposits similar in appearance to those obtained from the thermal decomposition of solutions of bisbenzenechromium, which appeared to be free of the green oxidised product. The chromium metal deposited was insoluble in cold or hot mineral acids; the amount of chromium deposited

THERMAL DECOMPOSITION OF ARENE CHROMIUM TRICARBONYLS

Paraffin, 5gm.	Arene, 5gm.	$Cr(CO)_6$	Decomposition Temperature °C.	Chromium Count x 10^3	Nature of Deposit
n-Octadecane	Tetralin	1 gm.	275	2	Green oxidised deposit
"	Naphthalene	"	300	0·5	
"	Anthracene	"	320	1	
n Eicosane	Biphenyl	"	315	-	No deposit detected
n Octadecane	p Terphenyl	"	320	2	Visible traces of deposit
n Eicosane	m Terphenyl	"	305	4	
n Octadecane	t Stilbene	"	310	14	Even black metallic deposit
n Eicosane	"	"	325	33	
n Octadecane	diphenyl butadiene	"	310	6	
n Eicosane	"	"	335	25	
n Octadecane	bipyridyl	"	320	6	Thin, even black deposit
"	t Stilbene	$Cr(C_6H_6)_2$ 1 gm.	303	80	Thick, even metal deposit for comparison

on the alumina fibres was estimated by use of the electron probe microanalyser. The best fibre from each solution was scanned for chromium over several areas on its surface for a given time, and the "count" was recorded; the results are summarised in the table on page 75. The results confirmed the conclusion from microscopic examination, that the thermal decomposition of the t-Stilbene chromium tricarbonyl compound was the most effective of the methods examined for the deposition of chromium: this method was therefore examined in more detail.

The various factors which affect the process are described in the following pages: no quantitative experiments were performed on the system. In all cases the weight of solvent was 10gm. and the experiments were carried out in a 250 ml. round-bottomed flask heated by a mantle in the argon-filled glove-box, unless otherwise stated.

Effect of solvent:

According to the equation

$$Cr(CO)_6 + C_6H_5.CH : CH \cdot C_6H_5 \rightarrow (C_6H_5.CH:CH.\ C_6H_5)Cr\ (CO)_3 + 3CO$$

1gm. chromium hexacarbonyl reacts completely with 0.84gm. t-Stilbene.

When a solution of 1gm. chromium hexacarbonyl in a mixture of 1gm. t-Stilbene and 9gm. n-Octadecane was heated, a large proportion of the chromium hexacarbonyl sublimed out of the solution; after thermal decomposition of the solution, only a thin, patchy coating of chromium was formed on alumina fibres immersed in the solution, since only a small amount of t-Stilbene chromium tricarbonyl had been formed.

Undiluted t-Stilbene reacted strongly with chromium hexacarbonyl at 200°C, but was unsuitable as a solvent because of its high melting point and its tendency to sublime. An equal weight mixture of t Stilbene and paraffin hydrocarbon was the best solvent for the formation of the tricarbonyl compound and its subsequent thermal decomposition.

The three paraffins used, n-Octadecane, n-Eicosane and n-Docosane, were found to be equally effective, with the exception of n Octadecane at temperatures above 310°C; mixtures including this paraffin generally boiled between 310°C and 315°C.

Effect of Temperature:

The thermal decomposition of the t-Stilbene chromium tricarbonyl compound formed by heating 1 gm. chromium hexacarbonyl in 5 gm. t-Stilbene and 5 gm. n-Octadecane began between 310° and 315°C with the appearance of a black deposit. The decomposition appeared to be substantially complete within three minutes at 315°C, but some undecomposed yellow compound was found when the system was cooled to room temperature: however, since the liquid became completely black once thermal decomposition had begun the course of the decomposition reaction could not be followed by visual means alone.

The formation of t-Stilbene chromium tricarbonyl by the reaction between chromium hexacarbonyl and t-Stilbene in solution was adversely affected by the removal of chromium hexacarbonyl from solution by sublimation. The rate at which the tricarbonyl compound is formed increases as temperature increases; the rate at which chromium hexacarbonyl sublimes from solution also increases as temperature increases. Since the only way to return sublimed hexacarbonyl to the solution is to push it back with a rod, which is not very effective, the use of an intermediate temperature in the region of 200°C was found to give a satisfactory yield of the tricarbonyl compound prior to thermal decomposition.

Up to 0·2gm. of 1gm. chromium hexacarbonyl solute was found to be lost by sublimation at temperatures up to 330°C: this was collected, purified by recrystallisation from ethanol and used again.

Effect of Concentration:

The thermal decomposition of solutions of concentration less than 0·25gm. chromium hexacarbonyl in 10gm. solvent gave uneven, patchy deposits of chromium on alumina fibres immersed in solution, although no evidence of oxidation was found in the deposit. Solutions of concentration greater than 1gm. chromium hexacarbonyl in 10gm. solvent were not investigated.

Concentrations between 5 and 10 per cent. by weight gave the best results; examination of deposited chromium on silicon nitride whiskers from different concentrations indicated that the amount of chromium deposited was increased by increasing the initial concentration of chromium hexacarbonyl in the solution, although the quantitative nature of this increase was not determined because of the insolubility of the deposited chromium in mineral acids.

Effect of Stirring:

Gentle mechanical stirring increased the rate at which chromium hexacarbonyl sublimed out of the solution: at temperatures above 300°C it increased volatilisation of the solution and the deposition of chromium on the walls of the flask above solution from the vapour phase. However, when a large bulk of silicon nitride whiskers was suspended in the solution, it was seen that the deposition of metal on them began at the walls of the flask and spread inwards to the centre of the solution; to ensure even deposition in such a case, the suspension was stirred by hand with a long spatula as soon as metal deposition began at the flask walls: this method proved effective.

Effect of Protective Atmosphere:

Although chromium hexacarbonyl and t-Stilbene chromium tricarbonyl are relatively stable to oxidation by air, the need for an inert protective atmosphere was established by performing the thermal decomposition of a solution in air; the only product found was green chromic oxide heavily contaminated with organic matter.

Effect of Substrate:

The thermal decomposition of a solution of 1gm. chromium hexacarbonyl in 5gm. t-Stilbene, 5gm. n-Octadecane at 315°C has led to the deposition of a thin layer of chromium metal on the surfaces of the following solid objects: activated alumina, polycrystalline alumina fibres, gold, glass, mica, silicon carbide whiskers and silicon nitride whiskers.

i) Activated Alumina:

Chromatographic lump alumina was activated at 300°C : 0·5gm. was immersed in the solution. The thermal decomposition of the solution deposited a thick layer of chromium on the lumps, and lowered the amount of chromium metal powder produced homogeneously in the solution.

ii) Polycrystalline Alumina Fibres:

The fibres became coated with an even, black layer of chromium metal; a large amount of metal powder was also formed by homogeneous decomposition in the solution. The thickness of the chromium deposit was between 0.5 and 1 micron.

iii) Gold:

A rectangular block of gold was polished, buffed to a very shiny finish, and immediately immersed in the solution to ensure that an oxide-free metal surface was in contact with the solution. Thermal decomposition of the solution gave a thin, even, blue-black shiny deposit of chromium on the surface of the gold block.

iv) Glass:

The glass vessel in which the thermal decomposition of the solution was carried out became coated with a layer of black chromium metal which formed a mirror in contact with the glass; this layer could be removed only by scouring with a commercial detergent abrasive, and was impervious to attack by mineral acids.

v) Mica:

A thin, freshly-cleaved sheet of mica was coated with a very thin, even, transparent layer of dark grey chromium by thermal decomposition of the solution in which it was immersed.

vi) Silicon carbide and silicon nitride whiskers:

In each case, 0·1gm. of whiskers was dispersed in the solution by stirring: thermal decomposition of the solution gave a deposit of chromium on the whiskers which was nodular in appearance. The deposit on most whiskers examined microscopically covered the whiskers completely.

The Nature of t-Stilbene chromium tricarbonyl:

Although the formation of a deposit of solid chromium from solution takes place by the decomposition of the t-Stilbene chromium tricarbonyl compound formed between chromium hexacarbonyl and t-Stilbene in solution, the overall reaction process

$$\text{t-Stilbene} + Cr(CO)_6 \longrightarrow (\text{t-Stilbene})Cr(CO)_3 + 3CO$$

$$(\text{t-Stilbene})\ Cr(CO)_3 \longrightarrow \text{t-Stilbene} + Cr + 3CO$$

may be represented by the equation

$$Cr\ (CO)_{6\ \text{solution}} \longrightarrow Cr_{\text{solid}} + 6\ CO_{\text{gas}}$$

so that any solvent which allowed the reaction represented by the last equation to proceed, to form a satisfactory deposit of chromium metal on a solid object immersed in the solution without contamination by carbon or oxygen, would be suitable for the process.

The various tricarbonyl compounds studied were prepared by heating a mixture of chromium hexacarbonyl and an excess of the relevant arene in diglyme under reflux in nitrogen, and isolating the solid compound; the Ultra-Violet absorption spectra of these compounds in very dilute ethanol solutions were compared with those of chromium hexacarbonyl, the original arenes, and the appropriate residual solutions after thermal decomposition: the spectra of the arene hydrocarbons and their tricarbonyl derivatives are compared in Figures 6 to 8

Arene chromium tricarbonyl compounds generally have a characteristic peak in their absorption spectra between 300 and 325 mμ; as the molecular weight of the arene increases and its delocalised π-orbital system is extended, the peak becomes less evident. Both t-Stilbene and 1,4 diphenyl buta 1,3 diene have wide absorption peaks between 275 and 325 mμ;

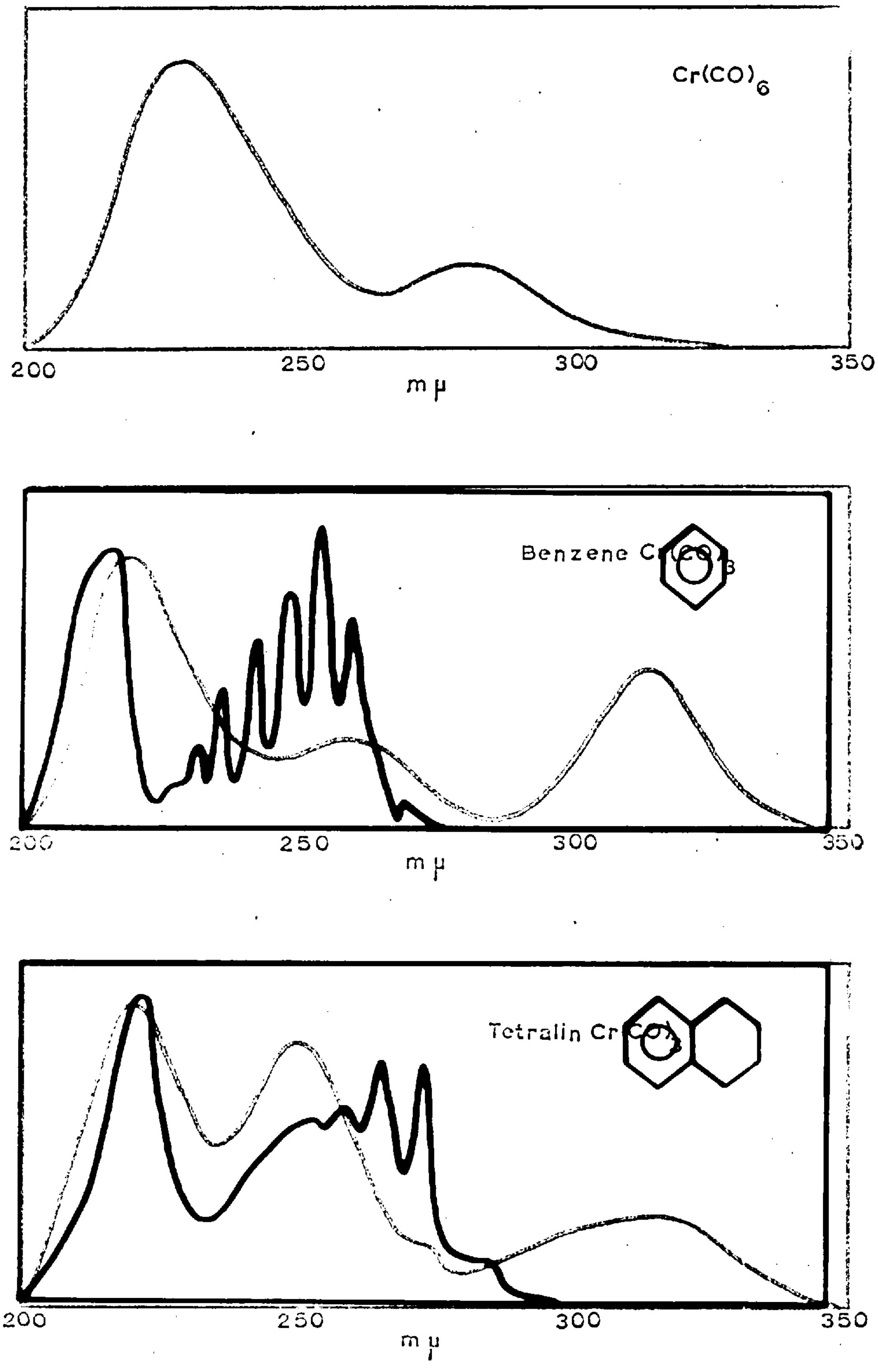
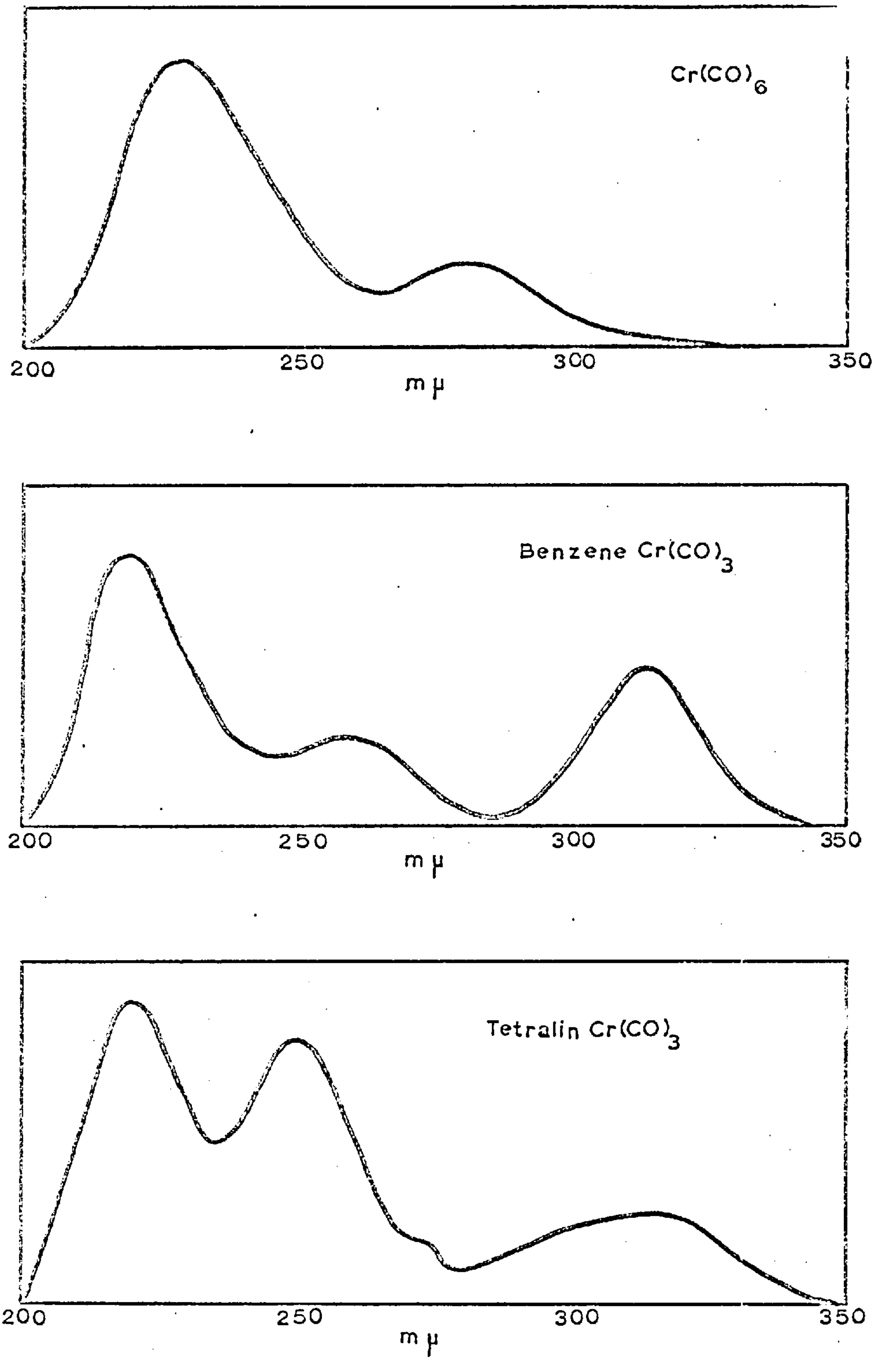

Cr(CO)6
200
250
300
350
mμ
Benzene Cr(CO)3
200
250
300
350
mμ
Tetralin Cr(CO)3
200
250
300
350
mμ

Fig.6.


$Cr(CO)_6$
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Benzene $Cr(CO)_3$
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Tetralin $Cr(CO)_3$
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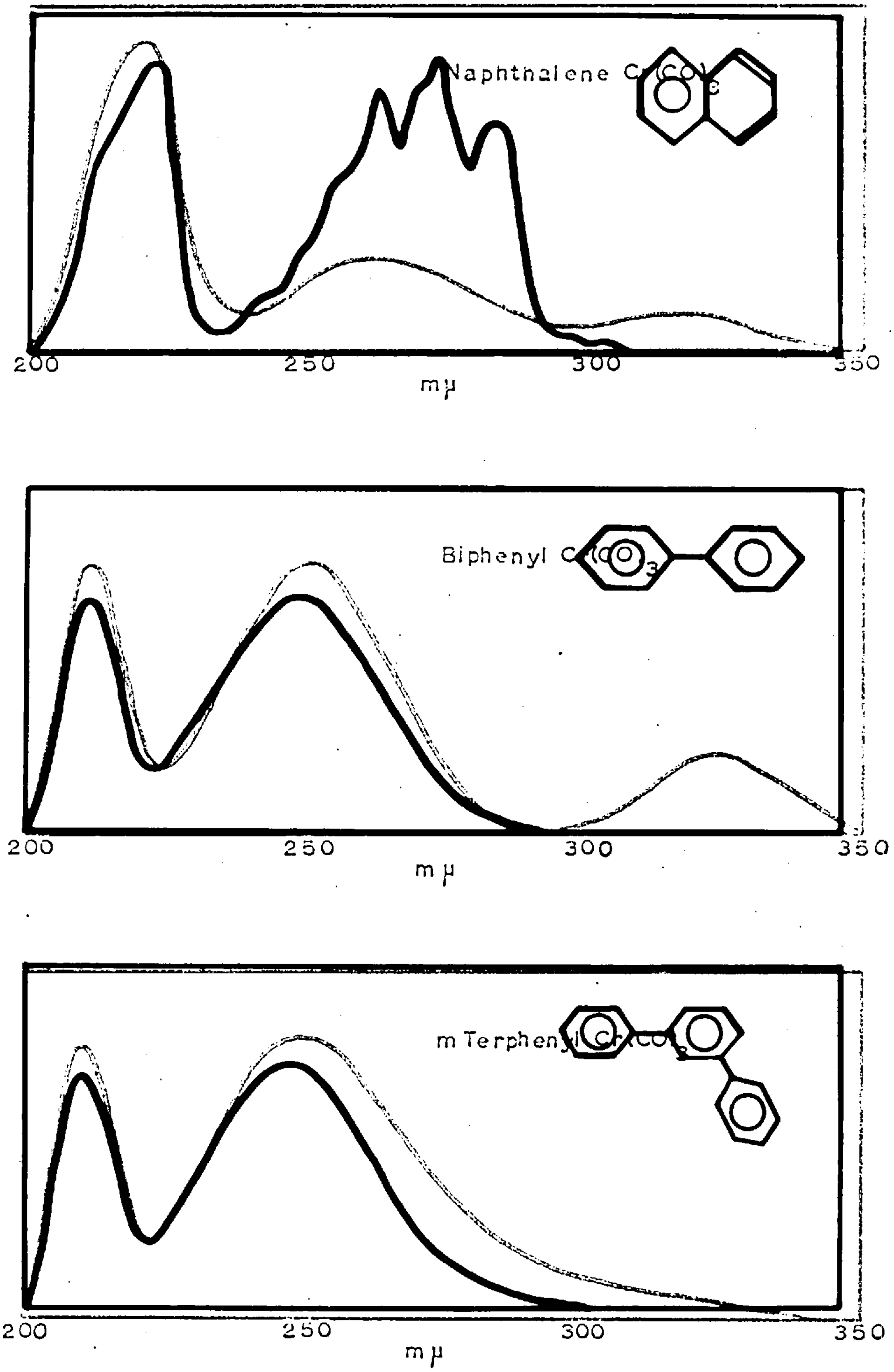
Fig.6.


Naphthalene Cr(CO)$_3$
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Biphenyl Cr(CO)$_3$
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m Terphenyl Cr(CO)$_3$
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250
300
350
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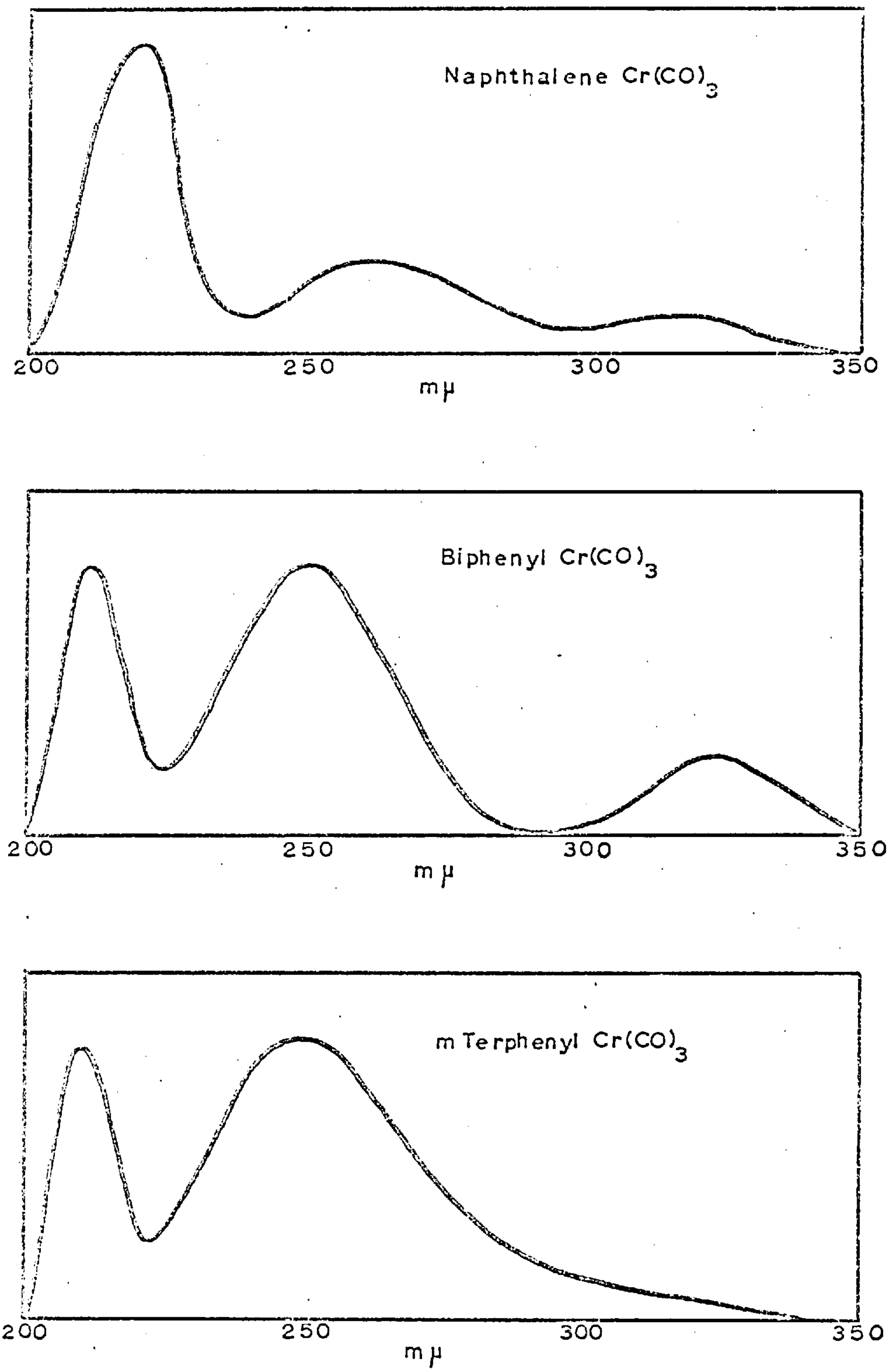
Fig. 7.


Naphthalene $Cr(CO)_3$
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Biphenyl $Cr(CO)_3$
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350
mμ

Fig. 7.

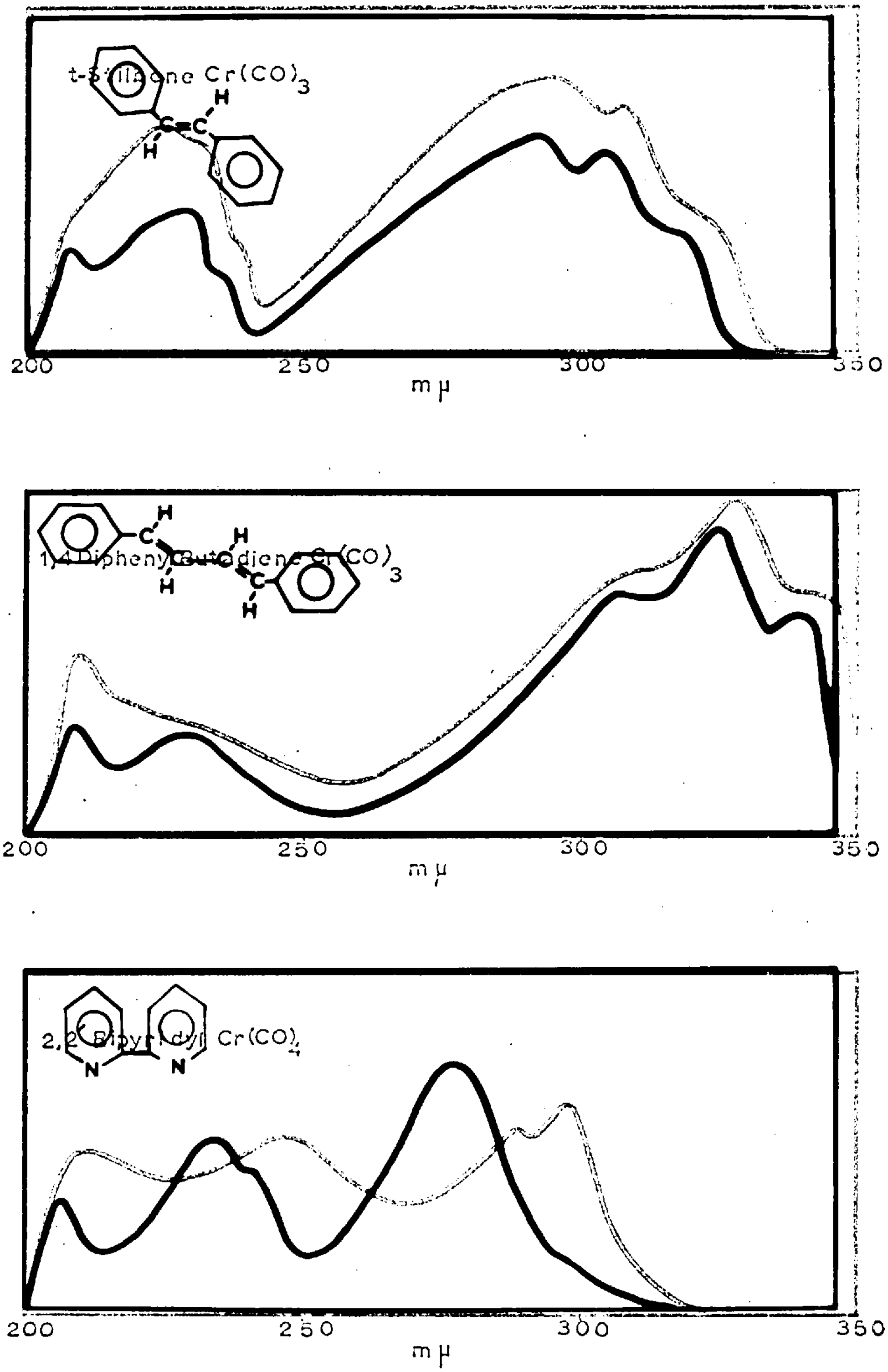

t-Stilbene Cr(CO)$_3$
H
C=C
H
200
250
300
350
mμ
1,4 Diphenyl Butadiene Cr(CO)$_3$
H
C
C
H
H
C
C
H
200
250
300
350
mμ
2,2' Bipyridyl Cr(CO)$_4$
N
N
200
250
300
350
mμ

Fig. 8.

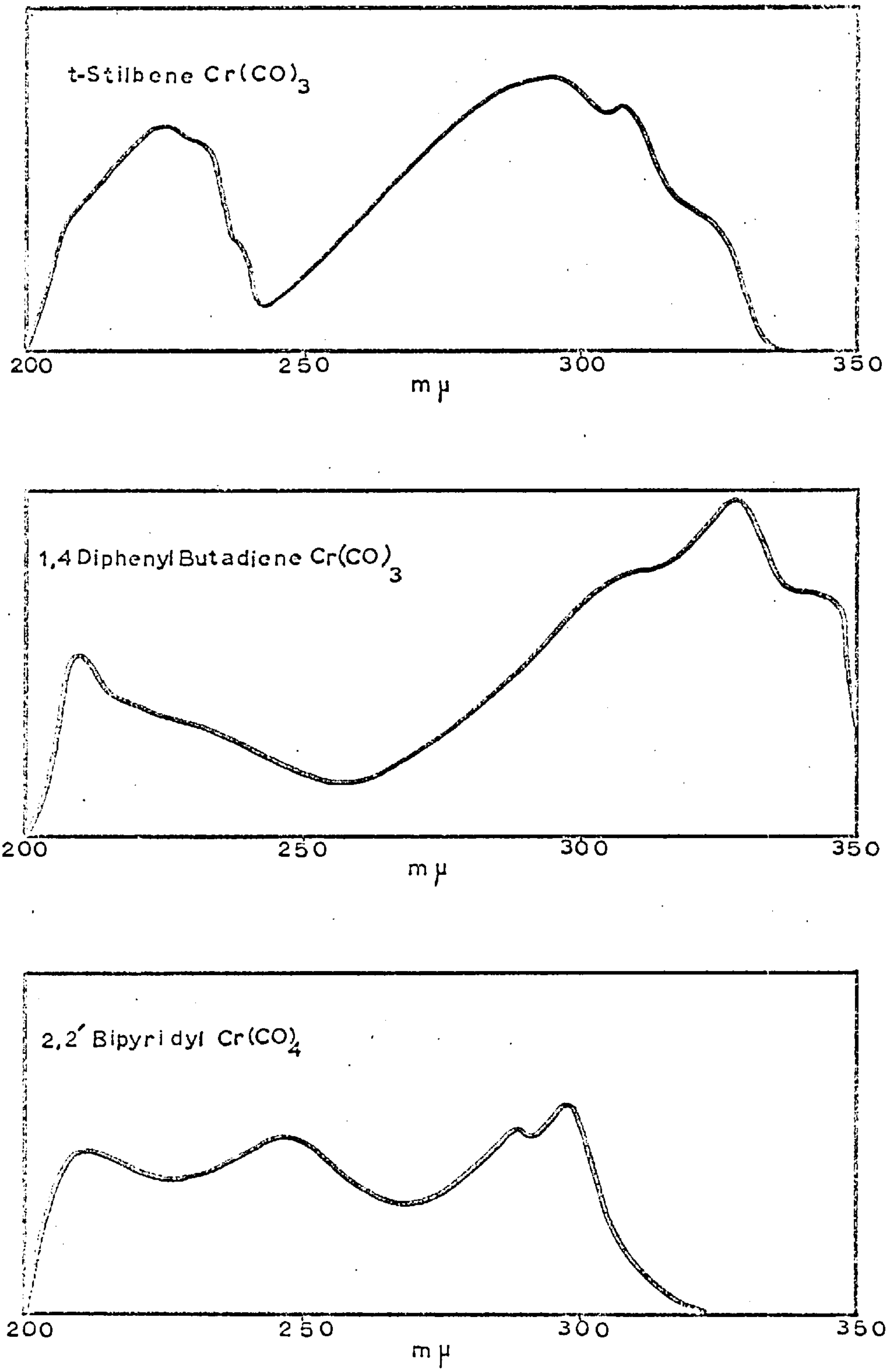

t-Stilbene Cr(CO)3
200
250
300
350
mμ
1,4 Diphenyl Butadiene Cr(CO)3
200
250
300
350
mμ
2,2′ Bipyridyl Cr(CO)4
200
250
300
350
mμ

Fig. 8.

no new peaks appeared in the spectra of the tricarbonyl chromium derivatives of these arenes. Attempts to determine the molar extinction coefficients of the arene chromium tricarbonyl compounds were unsuccessful because of the instability of the compounds in the very dilute solutions in ethanol used in their spectroscopic examination; the compounds appeared to be oxidised to an ethanol-insoluble product which formed a cloudy film on the surfaces of the quartz cell.

All the solid arene chromium tricarbonyl compounds were found to be decomposed by air over a period of several days to form a green species insoluble in organic solvents.

Comparison of the numerous peaks in the Infra-Red spectrum of t-Stilbene chromium tricarbonyl with those recorded for other arene chromium tricarbonyl compounds(46) indicated that the nature of the bonding is the same in all compounds of this type, in that a benzene ring acts as a tridentate ligand to replace three of the six carbonyl groups in chromium hexacarbonyl; however, there is no conclusive evidence that the delocalised π-orbital of the benzene ring is localised to a cyclic triene configuration in these compounds. The bonding in these compounds therefore consists of both formal metal-carbon bonds joining chromium and the three carbonyl groups, and the 'sandwich-type' bonding joining chromium and the benzene ring, as found in bisbenzenechromium.

The Nature of the metal deposit

The thermal decomposition of solutions of t-Stilbene chromium tricarbonyl produced coatings of chromium metal on metallic and non-metallic solids immersed in the solutions; these chromium coating were electrically conducting, but insoluble in mineral acids, even after extensive washing of the specimens to remove organic impurities and boiling them in dilute acids for several days.

Electron probe microanalysis of chromium coated polycrystalline alumina fibres showed that the only detectable impurity in the chromium was carbon; the carbon content of the chromium was within the limit of detection of the instrument, but in no case was found to be present at >2 per cent. by weight. Chromium deposited from solutions heated to 335°C appeared to contain a higher carbon content than chromium deposited from solutions heated only to 315°C.

Electron probe microanalysis of chromium deposited on gold showed that elements with atomic number of 12 and above, apart from chromium and gold, were below the limit of detection of the instrument, which are 0•5 per.cent. for carbon, and 0•1 per.cent. for other elements. The chromium deposit on gold was therefore oxide free, and had a very low carbon content. No estimation of the carbon content in chromium deposited on silicon carbide or nitride whiskers was possible on this instrument.

Electron diffraction patterns from very thin whiskers with very thin chromium coatings taken in the electron microscope indicated that the deposited chromium had a very small grain size, and that there was no crystallographic relationship between the deposit and the single crystal whisker.

The difficulty encountered in removing chromium from the surfaces on which it had been deposited indicated that it was firmly bonded to those surfaces; the only method of removing the chromium deposit was by abrasion.

2,2' bipyridyl compounds formed by chromium hexacarbonyl:

According to the equation

$$Cr(CO)_6 + 3\ bipy \longrightarrow Cr\ (bipy)_3 + 6CO.$$

1gm. chromium hexacarbonyl reacts completely with 2gm. 2,2' bipyridyl to form tris - 2,2' bipyridyl chromium (0).(40)

A solution of 1gm. chromium hexacarbonyl in 5gm. 2,2' bipyridyl and 5gm. n-Octadecane was heated to 200°C for one hour; the solution became red, then black:

$$Cr(CO)_6 + bipy \longrightarrow \underset{(red)}{(bipy)Cr(CO)_4} + 2CO$$

$$(bipy)Cr(CO)_4 + bipy \longrightarrow Cr(bipy)_{3\,(black)} + 4CO.$$

The solution was then heated to 320°C for ten minutes, then cooled to room temperature; these reactions were carried out in the argon glove-box. Polycrystalline alumina fibres immersed in the solution were evenly coated with black, insoluble chromium metal of carbon content approximately one per.cent., but with no trace of contamination by nitrogen; in tris 22' bipyridyl chromium (0), the three bipyridyl molecules are bonded to the zerovalent chromium atom by their nitrogen atoms.

Since this method did not yield such a heavy deposit of chromium on the alumina fibres as the method using t-Stilbene, it was not investigated further. 1, 10-phenanthroline, which forms compounds with chromium hexacarbonyl analogous to those formed by bipyridyl, was not investigated.

Discussion:

The thermal decomposition of a solution of t-Stilbene chromium tricarbonyl in an equal weight mixture of t-Stilbene and a paraffin of boiling point above 305°C, formed by heating between 0·5 and 1gm. of chromium hexacarbonyl in 5gm. t-Stilbene and 5gm. paraffin in an inert atmosphere, will deposit a thin layer of reasonably pure chromium metal on both metallic and non-metallic solid surfaces immersed in the solution.

The advantage of this method over the thermal decomposition of solutions of bisbenzenechromium is that the starting material, chromium hexacarbonyl, is easier to obtain, store and handle than bisbenzenechromium; chromium hexacarbonyl may be stored in air in a dark bottle indefinitely without deterioration, and may be handled with ease in air, although it is toxic. Any chromium hexacarbonyl undecomposed because of its sublimation from solution can easily be recovered.

The thermal decomposition of t-Stilbene chromium tricarbonyl is slower than that of bisbenzenechromium, and so may in principle be controlled by controlling the time of the decomposition at the lowest possible temperature. The method does not result in the deposition of thick coatings of chromium on relatively large objects such as polycrystalline alumina fibres, and produces a large proportion of metal powder by homogeneous decomposition in solution in such cases. However, for the deposition of chromium onto whiskers the method of immersing the largest possible amount of whiskers in the solution, and stirring the suspension manually when metal deposition begins, so that all the whiskers receive a thin coating of chromium metal when the chromium compound in solution is totally decomposed, still appears to be the most efficient way of using such a process.

SECTION 3 : ALUMINIUM

The aluminium compounds which were considered to be potentially useful for the deposition of aluminium metal onto the surfaces of solid objects immersed in solutions of those compounds were:

i) Lithium aluminium hydride, ethereal solutions of which decompose at room temperature to produce aluminium powder;

ii) Aluminium trialkyls, which undergo thermal decomposition at temperatures above 240°C to produce aluminium metal;

iii) Tris - 2,2' bipyridyl aluminium (0), in which the formal oxidation state of the metal is zero; this compound has not been investigated.

All the work on aluminium described in this section was carried out in a glove-box with an oxygen-free argon atmosphere with a moisture content of less than 10 ppm. All apparatus was carefully dried before it was transferred to the glove-box.

THERMAL DECOMPOSITION OF LITHIUM ALUMINIUM HYDRIDE

Lithium aluminium hydride, (LAH), decomposes according to the reaction

$$\mathrm{Li\,Al\,H_4} \longrightarrow \mathrm{Li\,H + Al} + 1\tfrac{1}{2}\,\mathrm{H_2}$$

for which the standard Free Energy change at 25°C is

$$\Delta G^{o} = -3{\cdot}9 \text{ k cal/mole}$$

$$\text{and } \Delta H^{o} = +6{\cdot}8 \text{ k cal/mole}$$

when LAH, lithium hydride and aluminium are in the solid state.(47)

LAH is appreciably soluble in ethers of low boiling point;(48) solutions of LAH in diethyl ether decompose slowly and spontaneously according to the equation above. This decomposition is autocatalytic, and the presence of very finely divided aluminium, boron, copper, iron or silicon in suspension in the solution also catalyses the reaction.(49) The decomposition may also be catalysed by the spontaneous decomposition in the LAH solution of a small amount of titanium aluminium hydride (TAH), formed by the addition of a small amount of titanium tetrachloride in diethyl ether; TAH is stable only at low temperatures, and is normally prepared at - 110°C:(50)

$$\mathrm{Ti\,Cl_4} + 4\,\mathrm{Li\,Al\,H_4} \longrightarrow \mathrm{Ti\,(Al\,H_4)_4} + 4\,\mathrm{Li\,Cl}$$

$$\mathrm{Ti\,(Al\,H_4)_4} \longrightarrow \mathrm{Ti} + 4\,\mathrm{Al} + 8\,\mathrm{H_2}$$

The finely divided titanium and aluminium metal powder formed by this decomposition acts as nuclei for the decomposition of the remaining LAH in solution: although the decomposition is endothermic, it is believed to account for the explosions reported in the use of LAH solutions.

It was thought that whiskers might be small enough to catalyse the decomposition of LAH solutions to form a coating of aluminium on their surfaces.

Some preliminary qualitative experiments were performed on the decomposition of solutions of LAH in tetrahydrofurfuroxy-tetrahydropyran (T - solvent). Clear LAH solutions were prepared by stirring solid LAH into T-solvent, and filtering the suspension through a glass wool plug under suction into a flask.

A small matt of very fine alumina single-crystal whiskers was immersed in the LAH solution, and the flask was sealed; after three days a grey sediment of aluminium metal powder was visible on the bottom of the flask. The solid contents of the flask were washed, dried and examined microscopically: the aluminium metal powder formed by homogeneous decomposition in solution was in a very fine state of division, but there was no evidence of any metal deposition in the whiskers. When this experiment was repeated using silicon nitride whiskers the same result was obtained.

A clear solution of LAH in T-solvent was prepared, and a few drops of a solution of titanium tetrachloride in T-solvent were added; the formation of the grey sediment in the solution appeared to be faster than in the absence of the titanium tetrachloride, and the decomposition of the solution appeared to be complete within two days. Again, no deposit of metal was detected on the surface of the whiskers which had been immersed in the solution.

It was concluded that the very flat, smooth surfaces of the whiskers were not catalytically active in the decomposition of LAH solutions; if aluminium were to be deposited on whiskers by this method, the whiskers would first have to be activated by the application of a thin layer of metal which was catalytically active to the decomposition of LAH in solution. Therefore no further work was carried out on this system.

THE THERMAL DECOMPOSITION OF TRI-ISOBUTYL ALUMINIUM AND DI-ISOBUTYL ALUMINIUM HYDRIDE.

Aluminium trialkyls and dialkyl hydrides can be prepared directly by the reaction between aluminium metal, hydrogen and the appropriate olefin.(51) The reaction is carried out under pressure in the presence of some already prepared aluminium trialkyl:

$$\mathrm{Al} + 1\tfrac{1}{2}\,\mathrm{H_2} + 2\,\mathrm{Al}\,(\mathrm{Cn\ H2n} + 1)_3 \longrightarrow 3\,\mathrm{Al\ H}\,(\mathrm{Cn\ H2n} + 1)_2$$

$$\mathrm{Al\ H}\,(\mathrm{Cn\ H2n} + 1)_2 + \mathrm{Cn\ H2n} \longrightarrow \mathrm{Al}\,(\mathrm{Cn\ H2n} + 1)_3$$

To a certain extent these reactions are reversible, since aluminium trialkyls thermally decompose by a two-stage process.(52)

$$\mathrm{Al}\,(\mathrm{Cn\ H2n} + 1)_3 \longrightarrow \mathrm{Al\ H}\,(\mathrm{Cn\ H2n} + 1)_2 + \mathrm{Cn\ H2n}$$

$$\mathrm{Al\ H}\,(\mathrm{Cn\ H2n} + 1)_2 \longrightarrow \mathrm{Al} + 1\tfrac{1}{2}\,\mathrm{H_2} + 2\,\mathrm{Cn\ H2n}.$$

The thermal decomposition of aluminium trialkyls and triaryls in the gas phase has been the basis of some methods for the vapour deposition of aluminium metal.(17b) Tri-isobutyl Al (TIBA), a colourless, viscous liquid of specific gravity 0·74 which decomposes at temperatures below its boiling point under atmospheric pressure, has been the most successful aluminium trialkyl used, although it is less volatile than the aluminium trialkyls of lower molecular weight. All aluminium-alkyl compounds react violently with oxygen and water, but TIBA reacts far less vigorously than the corresponding methyl and ethyl compounds: solutions of TIBA in hydrocarbons, which contain less than 25 per cent. TIBA, are not pyrophoric in air.

TIBA undergoes thermal decomposition by a two-stage process: at temperatures between 50° and 150°C it decomposes to isobutene and di-isobutyl aluminium hydride (DIBAH):

$$\mathrm{Al}\left[(CH_3)_2\,CH.\,CH_2\right]_3 \longrightarrow \mathrm{Al\,H}\left[(CH_3)_2\,CH.\,CH_2\right]_2 + (CH_3)_2\,C{:}CH_2$$

at 250°C, DIBAH decomposes to aluminium, hydrogen and isobutene:

$$\mathrm{Al\,H}\left[(CH_3)_2\,CH.\,CH_2\right]_2 \longrightarrow \mathrm{Al} + 1\tfrac{1}{2}\,H_2 + 2(CH_3)_2\,C:CH_2$$

In the gas phase, for the reaction

$$\mathrm{TIBA} \longrightarrow \mathrm{DIBAH}$$

$$\Delta H = +15{\cdot}75 \text{ k cal/mole}$$

The products of the reaction

$$\mathrm{DIBAH}_{(gas)} \longrightarrow \mathrm{Al}_{(solid)}$$

include aluminium metal, a small amount of aluminium carbide, but no elemental carbon, in the solid phase, and in the gas phase: hydrogen, methane, ethane, ethylene, propane, propene, n-butane, n-butene, iso-butane and iso-butene.(53)

Experimental:

Since both TIBA and DIBAH are viscous liquids at room temperature, they were transferred and measured by pipette from their storage cylinders which were kept in the argon-filled glove-box. Reactions were carried out in a 250ml. round-bottomed flask with a removable lid, heated by a mantle.

2 ml. TIBA was transferred to the flask containing several polycrystalline alumina fibres; the flask was heated until the TIBA decomposed completely to form aluminium metal, at 250°C. The alumina fibres were found to be completely coated with a smooth layer of aluminium metal which adhered firmly to the fibre surface. The walls of the flask were extensively coated with aluminium which could be peeled from the walls as a thin, shiny, ductile foil. At temperatures above 100°C the contents of the flask were extremely volatile; the extensive deposition of aluminium on the walls of the flask indicated that the fumes visible in the flask at elevated temperatures were not those of isobutene, liberated by the decomposition of TIBA to DIBAH, alone.

TIBA is miscible with liquid hydrocarbons: a solution of 1 ml. TIBA in 20gm. n-Octadecane containing several polycrystalline alumina fibres was heated to 260°C, when the solution began to decompose and a deposit of light grey aluminium appeared: the decomposition appeared to be complete within one minute. Aluminium was deposited on the alumina fibres, the bulb of the thermometer immersed in the solution, and the walls of the flask both above and below the solution; some aluminium powder also remained suspended in the solution. A small amount of the aluminium deposited on the fibres and the thermometer could be wiped off, leaving a firmly adherent layer underneath; the portion which was easily removed was thought to be sedimented metal powder formed by homogeneous decomposition in solution.

0·1gm. of a matt of silicon nitride whiskers was immersed in a solution of 1 ml. TIBA in 10gm. n-Octadecane. The flask was heated slowly: at 100°C the contents of the flask had volatilised heavily. At 240°C the deposition of aluminium began at the walls of the flask, and gradually spread inwards towards the centre. Decomposition appeared to be complete within about one minute, but the portion of the matt of whiskers at the centre of the flask was not coated with aluminium. However, when this experiment was repeated, and the suspension was stirred with a spatula as soon as the decomposition had started, aluminium was seen to have been deposited evenly over the whole matt of whiskers. When the matt of whiskers from the latter experiment was examined microscopically, a large percentage of the whiskers was found to be evenly coated with aluminium.

The disadvantage of this method was that a large amount of aluminium metal powder was produced by homogeneous decomposition in solution, and the walls of the flask above the solution were heavily coated with aluminium from the vapour phase decomposition of TIBA and DIBAH. When the proportion of TIBA to n-Octadecane in such a process was increased it was easier to ensure deposition of aluminium over the whole volume of the solution, but the amount of aluminium lost by volatilisation was increased. When the proportion of TIBA to n-Octadecane was decreased, volatilisation from the solution was less, but it was harder to obtain an even decomposition over the whole solution: however, down to the lowest concentration examined, 0·25 ml. TIBA in 10gm. n-Octadecane, a reasonably good deposit of aluminium was obtained on a large proportion of the whiskers in the solution.

Rotating Disc Experiments:

A solution of 2 ml. TIBA in 30gm. n-Octadecane heated to 250°C deposited a layer of aluminium metal on the closed circular end of a polycrystalline alumina cylinder immersed to a depth of 2 mm. in the solution, both when the cylinder was stationary and when it was rotating at 105 r.p.m.

Although a smooth, even deposit of aluminium was formed on the disc rotating in the solution, the volatilisation of the solution was greatly increased over that from a static solution, so that the amount of aluminium deposited on the walls of the flask above the solution was also increased.

The approximate partition of aluminium metal from this experiment was as follows:

2 ml. TIBA is approximately equivalent to 200 mg. aluminium metal:

Al deposited on alumina cylinder = 20 mg.
Al powder suspended in solution = 50 mg.
Al deposited on flask walls = 100 mg.

To study the kinetics of the heterogeneous reaction whereby aluminium was deposited, it was necessary to measure the amount of aluminium deposited on the rotating disc. Since the deposition of aluminium on the flask walls could be regarded as a very variable error in this process, and the amount of aluminium lost in this way was greater than the amount which it was required to measure, this method was considered unsuitable for studying the kinetics of the process, and so no further rotating disc experiments were performed.

However, these experiments did indicate that continuous mechanical stirring was unsuitable for effecting even deposition of aluminium throughout the solution because of the increased volatilisation which it caused. Therefore the only form of stirring employed was manual stirring after the deposition of aluminium had begun.

Although the thermal decomposition of solutions of TIBA in n-Octadecane gave satisfactory deposits of aluminium on solid objects immersed in the solutions, the heavy deposition of aluminium on the flask walls above solution made the process inefficient.

DIBAH, formed by the partial decomposition of TIBA at temperatures between 50° and 150°C, is far less volatile than TIBA: preliminary experiments indicated that solutions of DIBAH, from a separate source, in n-Octadecane were also less volatile than the corresponding TIBA solutions, and that the thermal decomposition of DIBAH solutions took place more evenly and cleanly, and at a lower temperature, than in TIBA solutions.

It has been shown that the carbon content of aluminium produced by the thermal decomposition of pure liquid DIBAH increases as the temperature of the decomposition increases: at a decomposition temperature of 245°C the carbon content of the aluminium is 0·2 per cent. which corresponds to an aluminium carbide content of 0.8 per cent.; at a decomposition temperature of 340°C the carbon content of the aluminium rises to one per cent. which corresponds to a carbide content of four per cent.(52)

The thermal decomposition of DIBAH in solution in n-Octadecane generally begins at temperatures between 205° and 210°C ; by using the lowest possible decomposition temperature, the carbon content of the aluminium produced from DIBAH solutions was minimised.

Effect of Concentration:

Solutions of composition between 0·5 ml. and 2·0 ml. DIBAH in 10gm. n-Octadecane were found to give good deposits of aluminium on silicon nitride whiskers. An appreciable amount of aluminium metal was deposited on the walls of the flask above solution at the higher concentrations, but a more complete coating of the whiskers by aluminium was easier to achieve than at the lower concentrations. The temperature at which decomposition began appeared to increase as the concentration of the solutions decreased: a solution of 2 ml. DIBAH in 10gm. n-Octadecane began to decompose at 205°C, whereas a solution of 1 ml. DIBAH in 15 gm. n-Octadecane began to decompose at between 215° and 220°C. A low rate of heating to the decomposition temperature was found to cause less volatilisation, and gave a more even decomposition than a rapid rate of heating.

Effect of Solvent:

n-Octadecane, n-Eicosane and n-Docosane were found to be equally suitable as solvents for DIBAH; in principle any hydrocarbon of boiling-point higher than 250°C which does not react with DIBAH may be used as a solvent.

Dialkyl aluminium hydrides react reversibly with aliphatic hydrocarbons containing carbon-carbon double bonds:(54)

$$R_2\,Al\,H \;+\; Cn\,H2n \;=\; R_2\,Al\,(Cn\,H2n + 1)$$

At temperatures up to 100°C the equilibrium of this reaction lies well to the right of the equation : the reaction proceeds most rapidly with 1 - alkenes. Dialkyl aluminium hydrides also form addition compounds with certain aryl compounds.

On the assumption that the addition of a 1- alkene of high molecular weight to DIBAH, to form a trialkyl aluminium compound of higher molecular weight that TIBA, would decrease the volatility of the aluminium compound, the addition of the alkenes n-1-Octadecene and n-1-Eicosene to DIBAH in solution was attempted.

As a standard, a solution of 2·0 ml. DIBAH in 10gm. n-Octadecane containing 0·1 gm. silicon nitride whiskers was heated at a rate of 5°C per minute: deposition of aluminium began at 210°C. The contents of the flask were immediately stirred manually; the temperature of the solution was allowed to reach 235°C to ensure complete decomposition of DIBAH. When the whiskers were examined microscopically they were all found to be coated with an even layer of aluminium.

A solution of 2·0 ml. DIBAH in 5gm. n-Octadecane, 5gm n-Octadecene containing 0·1gm. whiskers was heated to 80°C; the temperature of the solution was allowed to rise to 110°C during the course of one hour; it was then heated at 5° per minute until deposition of aluminium began at 215°C, when the suspension was stirred. The decomposition left only a patchy deposit on the whisker matt; the aluminium deposited on individual whiskers was of poor, uneven quality. Although the amount of aluminium deposited on the walls of the flask was decreased, the amount of metal powder formed by homogeneous decomposition was increased.

An equivalent result was obtained when 5 gm. n-Octadecane, 5 gm. n-1-Eicosene was used as a solvent under the same conditions.

When pure n-1-Octadecene and n-1-Eicosene alone were used as solvents, the deposition of aluminium began at 220°C. The amount of aluminium deposited on the flask walls was markedly decreased, but the amount of aluminium powder formed was increased, and the quality and quantity of aluminium deposited on individual whiskers were greatly impaired.

A similar series of experiments was performed using 10 gm. of an equal weight mixture of n-Octadecane and an arene hydrocarbon as solvent. The effects of the various arenes are summarised below:

Biphenyl lowered the decomposition temperature to approximately 170°C, and reduced the amount of aluminium plated from the vapour phase. A thin even coating of aluminium was formed on polycrystalline alumina fibres from one solution, and on silicon nitride whiskers from another, but the amount of aluminium powder produced was greatly increased.

Para-diphenyl-benzene also lowered the decomposition temperature to about 170°C, reduced the amount of aluminium deposited on the flask walls, increased the amount of metal powder formed, and gave a thin, even coating of aluminium on polycrystalline alumina fibres and silicon nitride whiskers.

Trans-Stilbene and 1,4 diphenyl-buta- 1,3 diene did not affect the decomposition temperature of the solution, which remained at 210°C, and did not apparently decrease the amount of aluminium deposited on the flask walls. The amount of metal powder, however, was increased, and only a thin layer of aluminium was deposited on alumina fibres and silicon nitride whiskers; almost all the metal deposited on the polycrystalline alumina fibres could be removed by wiping.

2,2' bipridyl formed a blood-red complex with DIBAH; the solution was heated to 300°C but no aluminium was deposited. The complex was soluble in acetone, but decomposed rapidly in contact with air.

Since none of the solvents containing unsaturated hydrocarbons investigated improved the quality or quantity of aluminium deposited on whiskers or fibres, saturated paraffin hydrocarbons were established as the best solvents for the thermal decomposition of DIBAH.

When the volumes of solutions of the same concentration were increased, the amount of aluminium deposited on the flask walls from the vapour phase remained approximately constant; therefore the amount of aluminium lost in this way became a smaller proportion of the aluminium deposited from the solution as the volume of the solution was increased. However, the amount of stirring needed to ensure a complete and even deposition throughout the solution increased as the volume of the solution increased.

Nature of Deposit:

The thermal decomposition of solutions of DIBAH in paraffins of boiling point above 300°C deposited aluminium metal on non-metallic solid objects immersed in the solutions, including polycrystalline alumina fibres, the bulb of the glass thermometer, silicon nitride whiskers, silicon carbide whiskers and a rotating cylinder of polycrystalline alumina. In the case of all the larger objects which could be handled easily, the aluminium deposit consisted of an outer layer of loosely adherent metal, which could be easily removed by wiping, above a firmly adherent layer of metal.

After extensive washing of samples in a Soxhlet extractor with refluxing benzene to remove non-volatile hydrocarbon impurities, the aluminium deposit was found to be soluble in dilute hydrochloric acid. Aluminium was estimated gravimetrically by precipitation of aluminium oxyquinolate from solution by 8-hydroxyquinoline (see Analytical Methods). Within the limits of accuracy of this method, the aluminium metal was found to have a very high purity, but since only small samples were examined this method was not expected to give very accurate results.

Attempts to estimate the carbide content of the aluminium deposit by measuring the methane content of the hydrogen liberated, by dissolving the metal deposit in dilute hydrochloric acid, were unsuccessful.

Electron probe microanalysis for carbon in the aluminium deposit showed that the carbon content was below the limit of detection (0·5 per cent.) of the apparatus. It was therefore concluded that the carbon content of the aluminium was well below the tolerance level for the application for which the process was intended.

Electron microscope studies of very thin whiskers coated with aluminium by this method indicated that the metal deposit had a very small grain size, and that there was no crystallographic orientation relationship between the whisker and the metal deposited upon it.

Discussion:

The main disadvantages of the thermal decomposition of DIBAH in normal paraffin solutions as a method for the heterogeneous deposition of aluminium metal are the volatilisation from the solution which leads to the deposition of aluminium on the walls of the flask above the solution, and the production of aluminium powder by homogeneous decomposition of DIBAH in the solution.

However, as experimental techniques were improved, good coatings of aluminium on whiskers were obtained through heterogeneous decomposition, and the amount of aluminium lost by volatilisation was reduced by the use of more dilute solutions. It is expected that as the decomposition is performed on increasingly larger scales, and experimental techniques improve, the process will become more efficient.

The aluminium deposited by this method was at least 99·5 per cent. pure, and appeared to adhere firmly to surfaces on which it was deposited. No chemical modification of the method has yet been found to improve the method.

SECTION 4.

Operating instructions for the two methods of depositing chromium and the method for depositing aluminium described previously are summarised as follows:

CHROMIUM.

Method 1 : Thermal Decomposition of Bisbenzenechromium (0).

i) A solid mixture of proportions 1gm. bisbenzenechromium, 5gm. n-Octadecane, 5gm. t-Stilbene, is prepared: the amount of this mixture should be such that it covers completely in the liquid state any solid object to be coated with chromium which is immersed in the mixture. Wherever possible, bisbenzenechromium should be handled in an inert atmosphere to avoid its oxidation.

ii) The mixture is heated in a glass vessel to between 302°C and 305°C for five minutes under a dry, oxygen-free inert gas atmosphere, and is then allowed to cool to room temperature.

iii) Solid objects immersed in the mixture are removed, and washed extensively with a hot organic solvent of low boiling-point, preferably under reflux in a Soxhlet extractor, to remove organic impurities: if the objects are relatively large and easy to handle, a layer of sedimented chromium powder may be wiped from the specimens. A layer of black, insoluble chromium metal of thickness between 1 and 5 microns may be deposited on metallic or non-metallic solids by this method.

Method 2 : Thermal Decomposition of trans-Stilbene chromium tricarbonyl.

i) A solid mixture of proportions 1gm. chromium hexacarbonyl, 5gm. n-Octadecane, 5gm. t-Stilbene is prepared, of sufficient bulk to cover completely, when liquid, any solid object to be coated with chromium. Chromium hexacarbonyl is stable to oxidation by air, but is toxic,

ii) The mixture is heated under a dry, oxygen-free inert gas atmosphere in a glass vessel to 200°C for at least one hour: chromium hexacarbonyl which sublimes our of solution should be returned manually with a glass rod or metal wire.

iii) The mixture is then heated to between 310°C and 315°C for ten minutes, and is then allowed to cool to room temperature.

iv) The objects coated with chromium are removed from the mixture, washed and dried. By this method a black,acid-insoluble layer of chromium metal of thickness up to 1 micron may be deposited on metallic or non-metallic solids.

The chromium deposited by both methods may be contaminated with up to 2 per cent. carbon, but is free from any other chemical impurity, including oxygen. The chromium has a very small grain size, adheres firmly to the surface on which it has been deposited, and resists corrosive attack by mineral acids.

ALUMINIUM

Thermal Decomposition of Di-isobutyl Aluminium Hydride.

i) A mixture of proportions between 0·5 ml. and 2·0 ml. DIBAH in 10gm. n-Octadecane is prepared at room temperature : DIBAH must be handled in a dry, oxygen-free atmosphere.

ii) The mixture is heated slowly to between 210°C and 215°C for five minutes, and is then allowed to cool to room temperature.

iii) Solid objects immersed in the mixtures are removed, washed and dried.

A layer of firmly adherent aluminium of purity at least 99·5 per cent. may be deposited on solid objects by this method: the aluminium is soluble in dilute mineral acids. Deposits of thickness up to 5 microns have been formed on whiskers by this method.

The Handling of Whiskers:

Whiskers are generally supplied in the form of a matt, which has the appearance of a low-density cotton-wool. The lower the diameter, the greater the length: diameter ratio of the whiskers, the more difficult it is to separate the individual whiskers from each other in the matt: this is shown by the relative ease with which silicon carbide whiskers can be separated, compared with the difficulty of separating silicon nitride whiskers manually.

The simplest way of separating a matt of whiskers is to stir it in a viscous liquid: the more viscous the liquid, the more easily and quickly the whiskers become separated; suitable liquids are glycerol, silicone oils and microscope immersion oils. However, to avoid possible chemical contamination during a metal deposition process, the best technique of whisker dispension is to stir the matt directly into the solvent to be used in the process. The most commonly used solvent in this work was n-Octadecane; it had the advantage that, since its melting point is 29°C, a matt could be stirred into a partially melted mass of the paraffin which was viscous enough to disperse the whiskers.

After metal had been deposited upon them from an organometallic solution, whiskers were recovered by washing the solution with hot chloroform or acetone, and filtering the solution; after filtration the whiskers returned to the form of a matt. The matt was washed with refluxing benzene in a Soxhlet thimble; this removed only a small part of the powder metal, produced during the deposition process, which had become trapped in the matt.

The best method of separating coated whiskers and metal powder was found to be by stirring the matt at a high speed in a low-viscosity organic solvent such as chloroform, carbon tetrachloride or acetone until the whiskers were dispersed; the suspension was then allowed to settle. The finely divided metal powder was found to sediment more slowly than the coated whiskers; when a large proportion of the whiskers had settled, the liquid containing the metal powder was decanted. The sedimented whiskers were then stirred with more liquid to separate any remaining powder, which was again decanted. Any whiskers which separated from the decanted liquid were added to the whisker-rich suspension; this process was repeated until no further metal powder was seen to separate from the whiskers. When the whiskers were dried under vacuum they returned to the form of a matt.

Although silicon carbide whiskers are stronger than silicon nitride whiskers, and are thought to be potentially far more useful for strengthening, silicon nitride whiskers were studied much more extensively in this work because the behaviour of silicon nitride whisker matts was far more typical than that of silicon carbide whisker matts. The silicon carbide supplied was very coarse, and the matts were easily separated, whereas silicon nitride matts could not be separated manually to any useful extent: most whisker matts resembled the latter type. It is expected that, as the quality of the silicon carbide supplied improves, and its whiskers become more uniformly long and thin, the behavious of the whiskers in matt form will resemble more that of silicon nitride.

Analytical Methods

The difficulty in the direct estimation of chromium metal produced by the thermal decomposition of zerovalent compounds lay in dissolving the deposited metal; although the metal conducted electricity, it was not soluble in any of the mineral acids normally used, even after it had been washed extensively to remove involatile organic impurities. Electrolysis was not attempted as a method of dissolution because of the difficulty of supporting coated whiskers during the removal of the metal layer.

Non-destructive instrumental analysis such as X-Ray fluorescence and X-Ray diffraction gave only semi-quantitative results; fluorescence revealed that no element with an atomic number greater than twenty apart from chromium was present in the metal deposit. Debye-Scherrer powder diffraction photographs, with reference to the ASTM index, gave diffraction angles from which intensities and inter-planar distances corresponded with those of pure chromium, within the limits of accuracy of the method.

Electron-probe microanalysis was found to be the best method, since the instrument is capable of detecting impurities, down to concentrations of 0·1 per cent., with atomic numbers above twelve; by this method the only impurity found in deposited chromium was carbon, which can not be detected below a concentration of 0·5 per cent. The amount of carbon which the deposited chromium contained varied from below the limit of detection of the apparatus, for chromium deposited on gold, to approximately 2 per cent. for chromium on rough, non-metallic surfaces: in such cases carbon was estimated, but could not be measured very accurately.

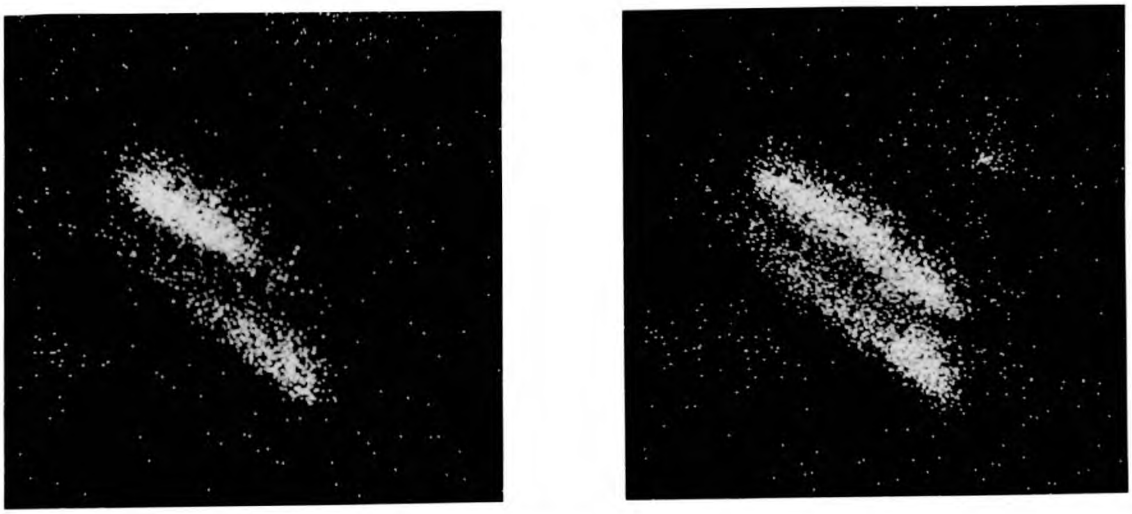
The aluminium deposited by the thermal decomposition of DIBAH was readily soluble in dilute hydrochloric acid when organic impurities had been removed; aluminium was assayed gravimetrically by the precipitation of aluminium oxyquinolate by the addition of 8 - hydroxyquinoline to aluminium solutions buffered by ammonium acetate.

Electron-probe microanalysis revealed no detectable impurities in the aluminium; this indicated that the carbon content of the deposit was less than 0·5 per cent. It was reported in the literature that carbon was estimated by dissolving deposited aluminium in dilute hydrochloric acid, and measuring the methane content of the hydrogen liberated by mass spectrometer. Attempts to measure the methane content of hydrogen, evolved by dissolving aluminium deposits in hydrochloric acid, by gas chromatography was unsuccessful. The measurement of carbon dioxide liberated by heating specimens in a stream of oxygen as a method of determining the carbon content of aluminium has been proposed; the carbon dioxide is trapped in a vessel cooled by a mixture of solid carbon dioxide and acetone. When combustion of the specimen is complete, the trapped carbon dioxide is allowed to evaporate and is passed through the gas chromatography column and measured; the apparatus for this method has not yet been completed.

While electron probe microanalysis is not a completely satisfactory method of analysis because it does not give an accurate quantitative value for the purity of the metals deposited by the methods described in this thesis, it does indicate that the only appreciable impurity in deposited chromium is carbon, which may be present up to 2 per cent. by weight, and that deposited aluminium contains no impurities which can be detected by this method.

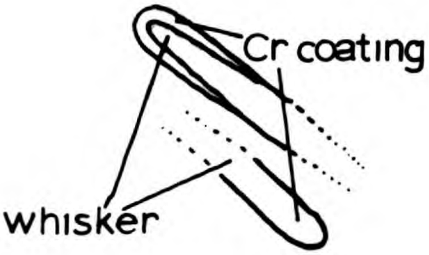
Optical microscopy proved to be a very useful method of qualitative analysis; the change in appearance between coated and uncoated whiskers was related to the presence of a metal coating on the whiskers by the following method:

Electron Probe Microanalysis



Si Trace

Cr Trace

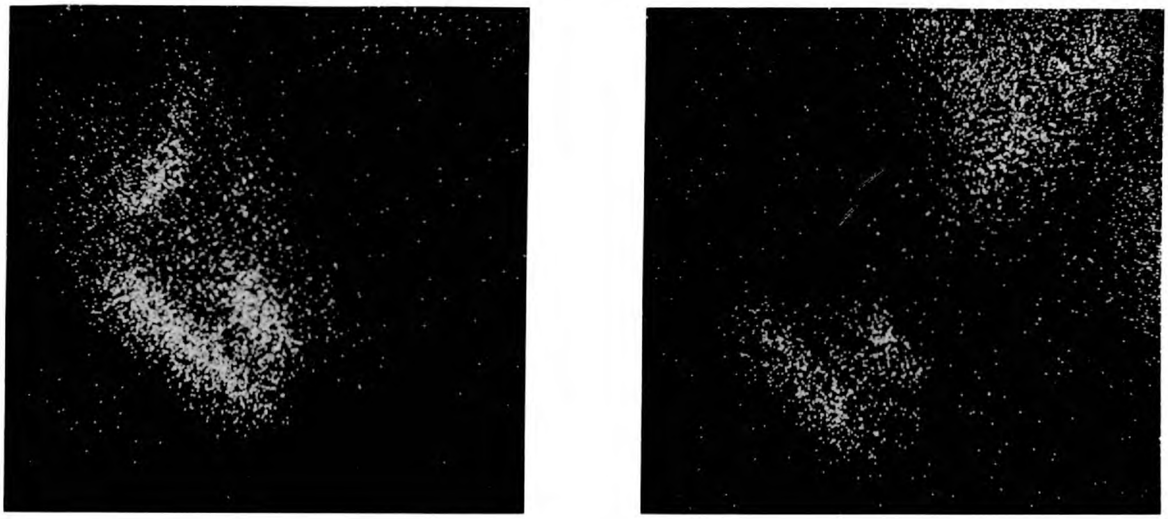


Optical Appearance

Magnification X 2,000

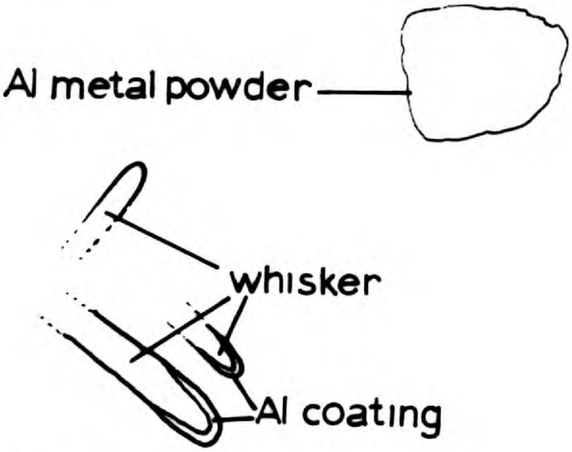
Fig. 9.

Electron Probe Microanalysis.



Si Trace

Al Trace



Optical Appearance

Magnification X 2,000

Fig. 10.

Optical Micrographs

Plate 6

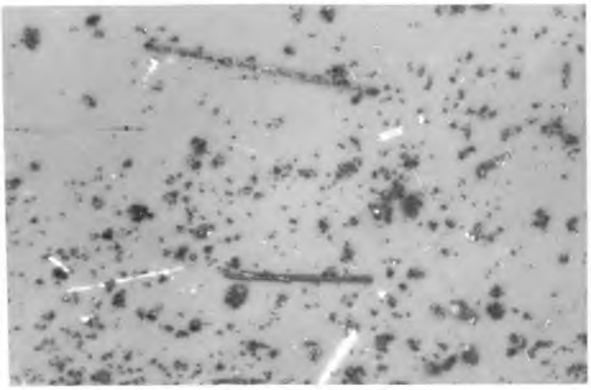
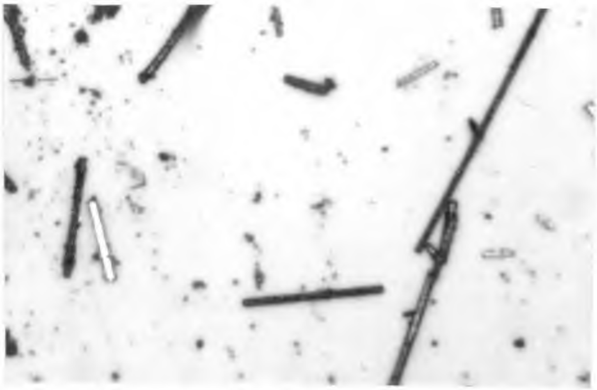


Plate 7



Cr on SiC + Cr powder before separation by sedimentation.

Cr on SiC after sedimentation.

Magnification X 625.

Plate 8

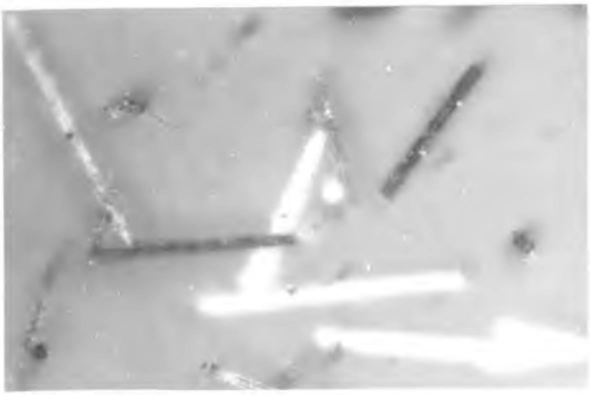
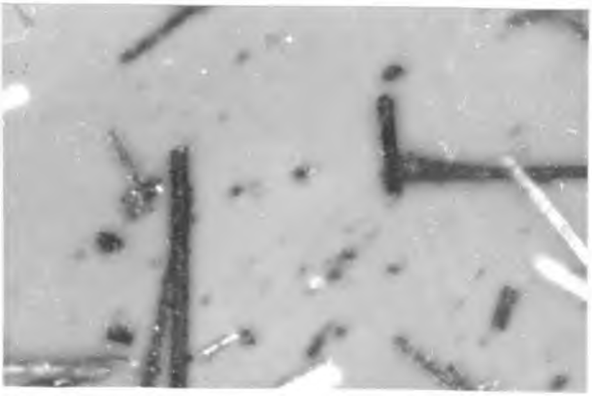


Plate 9



Cr on SiC (black) with bare SiC (white).

Cr on SiC (black) with bare SiC (white).

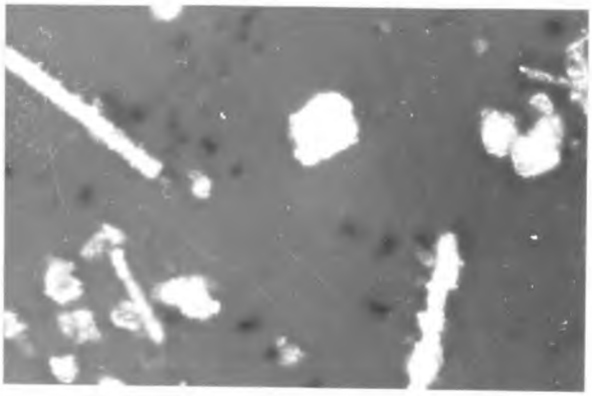
Magnification X 800

Optical Micrographs.

Plate 10

Al on Si_3N_4.

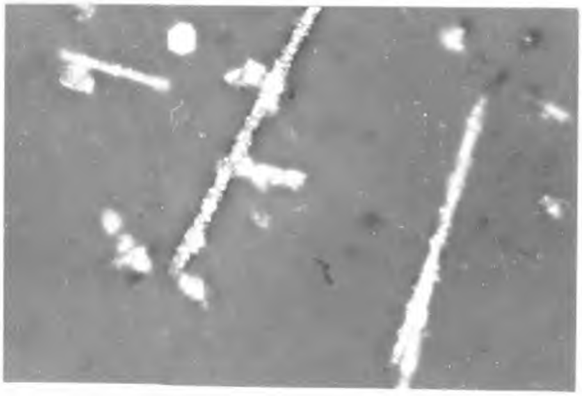
Plate 11



Al on SiC

Magnification X 625.

Plate 12



Al on SiC

Plate 13

Al on SiC

Magnification X 625.

A small amount of a matt of whiskers which appeared to be coated was dispersed in a mounting resin mixture which was then allowed to set, so that the resin contained randomly dispersed whiskers. The specimen was then polished, and examined periodically, until coated whiskers were observed at the surface of the specimen. This area of the specimen surface was scanned in the electron probe microanalyser for the silicon in the whisker and the metal with which the whisker was thought to be coated. The appearance of a heavy trace for both silicon and the metal at the same position on the surface of the specimen in the presence of a low surrounding background for both elements confirmed that whiskers with this appearance were in fact coated with metal: an optical photograph of the whiskers being scanned could not be obtained under these conditions. Typical results are shown in Figures 9 and 10.

The examination of coated and uncoated whiskers by electron microscopy was unsuccessful, mainly because the whiskers were too thick to be transparent to the electron beam; transparent specimens are generally less than 1,000 Å thick, and most of the whiskers examined were at least ten times thicker than this. No method of obtaining thin sections of whiskers was available.

Small samples of whiskers were mounted by floating a sample on the surface of water, and bringing a copper mounting grid up to the whiskers from below the surface of the water and catching the whiskers on the grid: the sample was then sandwiched between the grid on which it had been caught and another grid of the same size.

Generally the only images obtained in the electron microscope were the outlines of the whiskers; these confirmed the optical microscope findings that silicon nitride whiskers were very smooth and fine, but silicon carbide whiskers varied from relatively smooth to very rough surfaces. The outlines of coated whiskers showed that in most cases the whiskers were fairly evenly coated with metal with a surface which was considerably less smooth than that of the whiskers underneath.

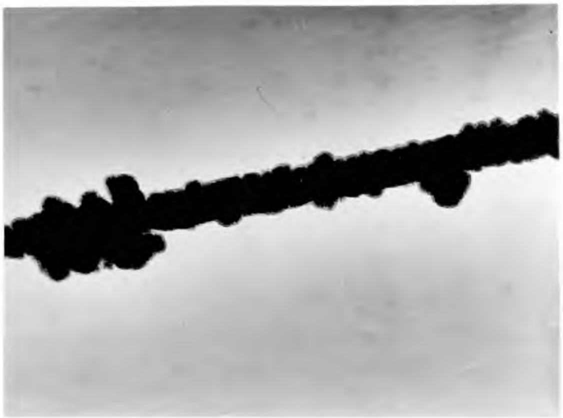
Selected area diffraction patterns were obtained only from extremely thin whiskers with or without very thin metal coatings. The single crystal nature of uncoated whiskers was confirmed by the distinct pattern of spots formed by diffraction of the electron beam by individual whiskers. Diffraction patterns from thinly coated thin whiskers indicated that the metal deposit had an extremely small grain size and that there was no epitaxial crystallographic relationship between the whisker and the deposited metal; this was shown by the diffraction pattern of the metal, as unbanded circles, superimposed on the single crystal diffraction pattern, as an orderly array of spots. If there were any large grain growth of the deposited metal, or any crystal relationship with the whisker, the two diffraction patterns would be expected to be related in some way. This evidence is not conclusive, however, since the whiskers from which diffraction patterns were obtained were considerably thinner than the average whiskers examined.

Electron Micrographs

Plate 14

Cr on Si_3N_4 whisker X20k

Plate 15



Cr on SiC whisker X30k

Plate 16

Selected Area Diffraction

Pattern from Plate X 15

Plate 17

Al on Si_3N_4 whisker

and bare whiskers.

DISCUSSION

The work described in this thesis is qualitative, and is concerned only with the establishment of methods for the heterogeneous deposition of metals, The main defect in all the methods examined is the significant amount of metal produced by homogeneous decomposition in the solution; there is no immediately apparent way of activating the surface of whiskers to the heterogeneous reaction so that the homogeneous reaction is decreased. The heterogeneous reaction appears to be independent of the chemical nature of the surface on which it occurs, since it takes place equally well on metallic and non-metallic surfaces. The amount of metal deposited heterogeneously on a surface will be directly proportional to the area of that surface under given conditions, so that the simplest way of increasing the amount of metal deposited heterogeneously, at the expense of that deposited homogeneously, is to increase the area of the surface to be coated in the solution.

The compounds of chromium studied may be regarded as consisting of chromium in an oxidation state of zero associated with certain ligands; on thermal decomposition the compound dissociates into chromium metal and the ligands. This decomposition is thought to be thermodynamically irreversible, since a very rapid dissociation occurs above a certain critical temperature. If the dissociation were reversible, it would occur slowly at temperatures just below the critical temperature;

no such slow decomposition has been observed. It seems more likely that the molecule dissociates because at the critical temperature its internal vibrational energy increases in such a way that the molecule enters a higher energy level in which the molecule dissociates into metal plus ligands.

When a zerovalent chromium compound in solution decomposes, the ligands are either soluble in the solvent or escape from solution as gas; the chromium metal produced may be deposited on homogeneous nuclei in solution or on heterogeneous surfaces with which the solution is in contact; effective deposition reactions are those in which the amount of metal deposited heterogeneously is a significant proportion of that deposited homogeneously. There is strong evidence that both bisbenzene-chromium and t-Stilbene chromium tricarbonyl associate with t-Stilbene in the equal-weight mixtures of t-Stilbene and n-Octadecane used as solvents, so that the metal compound becomes solvated: this **solvation** should have a marked effect on both homogeneous and heterogeneous reactions. Solvation will generally stabilise the compound against homogeneous nucleation: its effect on the heterogeneous reaction will be somewhat more complicated, since it occurs in five distinct steps:

1) Transport of the metal compound to the surface:
2) Adsorption of the compound on the surface
3) Dissociation of the compound to metal and ligands
4) Desorption of the ligands from surface
5) Transport of ligands away from surface

It is reasonable to assume that the last three stages of the heterogeneous reaction are unaffected by solvation of the metal compound.

Solvation of the metal compound infers that the compound will exist in solution as an effectively larger molecule whose diffusion coefficient will be lower than that of an unsolvated molecule under given conditions, so that less of the solvated molecule will be transported to the heterogeneous reaction surface in unit time. Therefore solvation will hinder the heterogeneous reaction rather than encourage it.

Adsorption is a very significant step in the heterogeneous reaction, since the metal is produced at a specific surface and must subsequently adhere to that surface. No data are available on the relative adsorption of alkyl hydrocarbons and aryl hydrocarbons on surfaces, but it is reasonable to assume that there is a greater interaction between any given surface and an unsaturated hydrocarbon than between the surface and a saturated paraffin hydrocarbon, because of the greater polarisability ~~flexibility~~ of the π-orbitals in the former than the σ-orbitals of the latter hydrocarbons, especially in the case of a fully conjugated arene hydrocarbon such as t-Stilbene. Therefore the metal compound may be expected to adsorb more readily on a solid surface if that surface is already associated with, and wetted by, the unsaturated hydrocarbon with which the metal compound is solvated in solution. Whether the large molecule, formed by solvation of the compound by the arene hydrocarbon, displaces the solvent arene hydrocarbon adsorbed on the solid surface completely, or whether the metal compound dissociates from the arene in solution and associates with the arene adsorbed on the surface, prior to thermal decomposition, is not known. It is therefore considered that the controlling factor in the heterogeneous reaction which deposits chromium is the adsorption of the metal compound on the surface.

Two factors must be considered in the thermal decomposition of arene chromium tricarbonyls: the adsorption of the metal compound onto heterogeneous reaction sites, and the decrease of the carbonyl character of the compound by the formation of a compound with strong π- bonded characteristics.

The carbonyl character of a compound in thermal decomposition is exhibited by chromium hexacarbonyl itself, which is thermally decomposed to chromic oxide and chromium carbide. An example of a compound with strong π-bonded characteristics is chlorobenzene chromium tricarbonyl; if chromium hexacarbonyl is heated in chlorobenzene, the compound $Cl\,C_6H_5\,Cr\,(CO)_3$ is formed. At temperatures above 130°C the compound decomposes to reasonably pure, oxide and carbide-free, chromium metal; strong association between the chlorobenzene solvent and the compound in solution is to be expected, but no heterogeneous reaction takes place, which infers that adsorption of the compound upon surfaces is not significant.

N.B. The Carbonyl Character referred to here implies the production of oxide and carbide rather than metal on the thermal decomposition of the compound in question.

Rigid polynuclear arene hydrocarbons such as Naphthalene, Anthracene and Phenanthrene, are effective in the deposition of small amounts of chromium contaminated with oxygen and carbon, which indicates that the chromium tricarbonyl compounds formed by these arenes have a predominantly carbonyl character, possibly because the hydrocarbons do not have completely delocalised π- orbitals. The results from these arene hydrocarbon compounds indicate that, although they do not dissociate cleanly to pure chromium, there is appreciable association between the compound and the solvent, and strong adsorption on solid surfaces in these systems.

Non-rigid polynuclear arene hydrocarbons which are fully conjugated, and have completely delocalised π-orbitals, such as t-Stilbene and 1,4 diphenyl butadiene, form chromium tricarbonyl compounds with little or no carbonyl character ; they are appreciably solvated in solution, and adsorb onto solid surfaces to give adherent, relatively pure chromium deposits on the surfaces.

Therefore the optimum conditions for the heterogeneous deposition of chromium require a zerovalent chromium compound with predominantly π-bonded characteristics, in a solvating solvent which also adsorbs on the solid surfaces on which chromium is to be deposited.

These principles, however, do not apply to the heterogeneous decomposition of di-isobutyl aluminium hydride, since the use of a solvent which associates strongly with the metal compound and which would be expected to adsorb on a surface more strongly than a normal paraffin appears to increase the amount of aluminium metal produced by homogeneous decomposition, and does not improve the quality or quantity of aluminium metal deposited heterogeneously: 1 - alkenes, which form the strongest compounds with DIBAH, may enhance the solvation of the resulting aluminium compound, but do not appear to improve its adsorption on solid surfaces.

It is possible that the decomposition of DIBAH to aluminium metal takes place by the formation of aluminium hydride, since TIBA decomposes to a hydride compound:

$$\underset{\text{TIBA}}{\mathrm{Al}\left[(\mathrm{CH_3})_2\,\mathrm{CH.}\ \mathrm{CH_3}\right]_3} \longrightarrow \underset{\text{DIBAH}}{\mathrm{H\ Al}\left[(\mathrm{CH_3})_2\ \mathrm{CH\ CH_3}\right]_2} + (\mathrm{CH_3})_2\ \mathrm{C{:}CH_2}$$

The mechanism of the further decomposition of DIBAH may be

$$\mathrm{H\ Al}\left[(\mathrm{CH_3})_2\ \ \mathrm{CH\ CH_3}\right]_2 \longrightarrow \mathrm{Al\ H_3} + 2\ (\mathrm{CH_3})_2\ \mathrm{C{:}CH_2}$$

$$\mathrm{AlH_3} \longrightarrow \mathrm{Al} + 1\tfrac{1}{2}\ \mathrm{H_2}$$

since the overall reaction is known to be

$$\mathrm{H\ Al}\left[(\mathrm{CH_3})_2\ \ \mathrm{CH\ CH_3}\right]_2 \longrightarrow \mathrm{Al} + 1\tfrac{1}{2}\ \mathrm{H_2} + 2\ (\mathrm{CH_3})_2\ \ \mathrm{C{:}CH_2}$$

Since the decomposition of TIBA to DIBAH is reversible, it is possible that the decomposition of DIBAH to aluminium at 210°C in n-Octadecane solution is also reversible, although it does not occur below a certain critical temperature; the change in decomposition temperature with change in concentration may indicate a tendency to reversible behaviour.

In order to interpret the mechanisms of these heterogeneous reactions more rigorously, data on the kinetics of the reactions are needed. Experiments should be performed on a quantitative basis to determine whether the heterogeneous reaction is controlled by transport or by the rate of decomposition of the compounds, which is another parameter which should be determined. Rotating disc experiments which were attempted failed completely for chromium, which did not deposit, and were not satisfactory for aluminium because of the large errors involved.

More precise methods of determining the extent of the impurities in the deposited metals should be developed and methods of minimising carbon contamination, which is thought to be the main impurity, should be found.

On the technical side, work is now in progress to increase the scale of the processes so that large amounts of whiskers may be coated in one solution, which, it is hoped, will make the processes more economical. A method of agitating a suspension of whiskers to ensure even deposition of metal without causing any appreciable increase in the volatilisation of the metal compound at high temperatures must be found; it is thought that a gentle raking action well below the surface of the solution would be effective in giving even deposition on a large scale.

This work has been successful in that new methods have been found for the deposition of chromium and aluminium on whiskers from solution, but the real success of this work will be revealed only when it is discovered if these methods of fabrication do improve the techniques of preparation, and the mechanical properties, of whisker-strengthened metals.

APPENDIX 1

The Pourbaix diagrams for the systems

Cr / H_2O , P/ H_2O, Al / H_2O

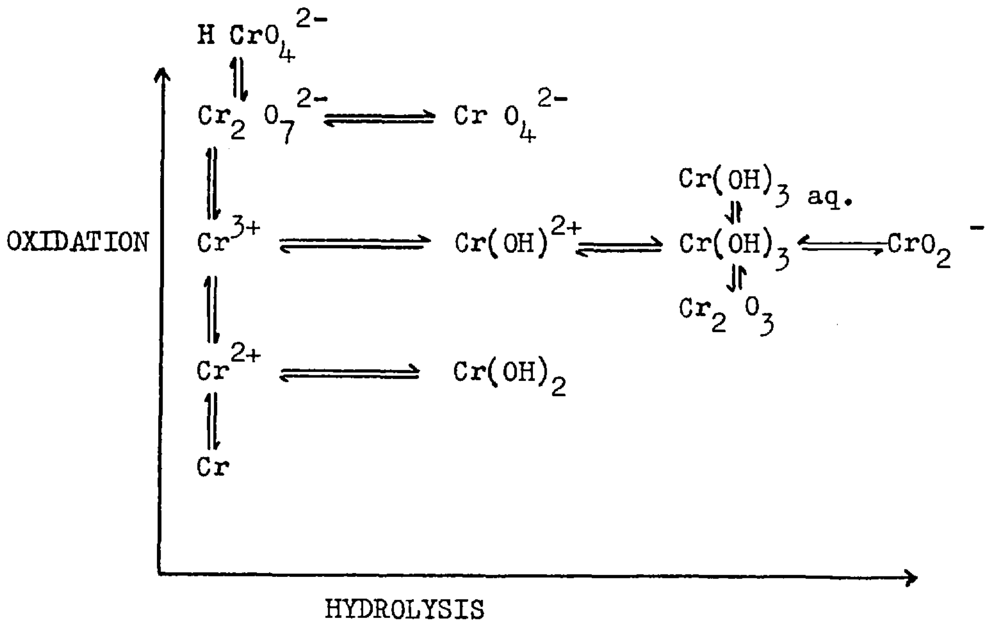
have been calculated from Free Energy of Formation data taken from Latimer. The following assumptions were made during the calculations:

1) The activity of all solid species was unity.
2) Each species in solution had the same constant activity.
3) Species existed only in the forms represented, with no complex formation:

CHROMIUM:

Species	ΔG^o kcal/mole	Species	ΔG^o kcal/mole
Cr	0	$Cr(OH)_3$ aq.	-205·5
Cr^{2+}	-42·1	$Cr O_2$	-130
$Cr(OH)_2$	-140·5	$Cr O_4^{2-}$	-176·1
Cr^{3+}	-51·5	$H Cr O_4^-$	-184·9
$Cr_2 O_3$	-250·2	$Cr_2 O_7^{2-}$	-315·4
$Cr O_2^-$	-125	$Cr O_3$	-121
$Cr(OH)^{2+}$	-103	H_2O	- 56·7
$Cr(OH)_3$	-215·3		

The simple aqueous chemistry of chromium is represented in the following diagram:



In the following equilibria, from which Figure 1 was calculated, the activity of each soluble species was taken as 10 $^{-2}$ molar.

Equilibrium	E volts
$Cr^{2+} + 2e = Cr$	- 0·97
$Cr(OH)_3 + 3H^+ + 3e = Cr + 3H_2O$	- 0·65 - 0·059 pH
$Cr_2O_3 + 6H^+ + 6e = 2Cr + 3H_2O$	- 0·58 - 0·059 pH
$Cr(OH)_3$ aq + $3H^+ + 3e = Cr + 3H_2O$	- 0·51 - 0·059 pH
$Cr(OH)_3 + 3H^+ + e = Cr^{2+} + 3H_2O$	- 0·02 - 0·177 pH
$Cr^{3+} + e = Cr^{2+}$	- 0·41
$Cr^{3+} = 3H_2O = Cr(OH)_3 + 3H^+$	pH = 2·21
$2Cr^{3+} + 3H_2O = Cr_2O_3 + 6H^+$	pH = 3·47
$Cr^{3+} + 3H_2O = Cr(OH)_3$ aq + $3H^+$	pH = 4·45
$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	+ 1·35 - 0·138 pH

$Cr_2O_7^{2-} + 8H^+ + 6e = 2Cr(OH)_3 + H_2O$	$+ 1{\cdot}22 - 0{\cdot}079$ pH
$Cr_2O_7^{2-} + 8H^+ + 6e = Cr_2O_3 + 4H_2O$	$+ 1{\cdot}15 - 0{\cdot}079$ pH
$Cr_2O_7^{2-} + 8H^+ + 6e = 2Cr(OH)_3aq + H_2O$	$+ 1{\cdot}08 - 0{\cdot}079$ pH
$Cr_2O_7^{2-} + H_2O = 2CrO_4^{2-} + 2H^+$	pH = $8{\cdot}4$
$CrO_4^{2-} + 5H^+ + 3e = Cr(OH)_3 + H_2O$	$+ 1{\cdot}31 - 0{\cdot}099$ pH
$2CrO_4^{2-} + 10H^+ + 6e = Cr_2O_3 + 5H_2O$	$+ 1{\cdot}23 - 0{\cdot}099$ pH
$CrO_4^{2-} + 5H^+ + 3e = Cr(OH)_3aq + H_2O$	$+ 1.14 - 0{\cdot}099$ pH

PHOSPHORUS

Species	ΔG^o kcal/mole	Species	ΔG^o kcal/mole
P	0	HPO_3^{2-}	- 194•0
H_3PO_2	- 125•1	H_3PO_4	- 274•2
$H_2PO_2^-$	- 122•4	$H_2PO_4^-$	- 271•3
H_3PO_3	- 204•8	HPO_4^{2-}	- 261•5
$H_2PO_3^-$	- 202•35	PO_4^{3-}	- 245•1

The simple aqueous chemistry of phosphorus is represented by the following diagram:

$$\begin{tikzcd}
H_3PO_4 \arrow[r] & H_2PO_4^- \arrow[r] & HPO_4^{2-} \arrow[r] & PO_4^{3-} \\
H_3PO_3 \arrow[u] \arrow[r] & H_2PO_3^- \arrow[r] & HPO_3^{2-} & \\
H_3PO_2 \arrow[u] \arrow[r] & H_2PO_2^- & & \\
P \arrow[u] & & &
\end{tikzcd}$$

Provided that the activity of each species in solution is the same, the only equilibria which are affected by the change in activity are those between solid phosphorus and hypophosphite: the activity of soluble species was therefore taken as 10^{-1} molar. The following equilibria are represented on the transparent sheet of Figure 1.

Equilibrium	E volts
$H_3PO_2 + H^+ + e = P + 2H_2O$	- 0·57 - 0·059 pH
$H_2PO_2^- + 2H^+ = e = P + 2H_2O$	- 0·45 - 0·118 pH
$H_3PO_2 = H_2PO_2^- + H^+$	pH = 1·98
$H_3PO_3 + 2H^+ + 2e = H_3PO_2 + H_2O$	- 0·50 - 0·059 pH
$H_2PO_3^- + 3H^+ + 2e = H_3PO_2 + H_2O$	- 0·45 - 0·088 pH
$H_2PO_3^- + 2H^+ + 2e = H_2PO_2^- + H_2O$	- 0·51 - 0·059 pH
$HPO_3^{2-} + 3H^+ + 2e = H_2PO_2^- + H_2O$	- 0·33 - 0·088 pH
$H_3PO_3 = H_2PO_3^- + H^+$	pH = 1.80
$H_2PO_3^- = HPO_3^{2-} + H^+$	pH = 6·17
$H_3PO_4 + 2H^+ + 2e = H_3PO_3 + H_2O$	- 0·28 - 0·59 pH
$H_3PO_4 + H^+ + 2e = H_2PO_3^- + H_2O$	- 0·32 - 0·029 pH
$H_2PO_4^- + 2H^+ + 2e = H_2PO_3^- + H_2O$	- 0·27 - 0·059 pH
$H_2PO_4^- + H^+ + 2e = HPO_3^{2-} + H_2O$	- 0·44 - 0·029 pH
$HPO_4^{2-} + 2H^+ + 2e = HPO_3^{2-} + H_2O$	- 0·23 - 0·059 pH

$PO_4^{3-} + 3H^+ + 2e = HPO_3^{2-} + H_2O$	$+ 0\cdot14 - 0\cdot088$ pH
$H_3PO_4 = H_2PO_4^- + H^+$	pH $= 2\cdot10$
$H_2PO_4^- = HPO_4^{2-} + H^+$	pH $= 7\cdot20$
$HPO_4^{2-} = PO_4^{3-} + H^+$	pH $= 12\cdot0$

ALUMINIUM:

Species	ΔG^o kcal/mole
Al	0
Al^{3+}	$- 115\cdot0$
$Al\ O_2^-$	$- 204\cdot7$
$H_2Al\ O_3^-$	$- 255\cdot2$
$Al_2\ O_3$	$- 376\cdot8$
$Al(OH)_3$	$- 271\cdot9$
H_2O	$- 56\cdot7$

The simple aqueous chemistry of aluminium is represented by the following diagram:

$$\begin{tikzcd}
Al^{3+} \arrow[r] & Al_2O_3 \arrow[r] \arrow[d, shift left] & AlO_2^- \arrow[d, shift right] \\
 & Al(OH)_3 \arrow[u, shift left] & H_2AlO_3^- \arrow[u, shift right] \\
Al \arrow[uu] & &
\end{tikzcd}$$

In the following equilibria, from which Figure 2 was calculated, the activity of each soluble species was taken as 10^{-2} molar.

Equilibrium	E volts
$Al^{3+} + 3e = Al$	- 1·70
$Al_2O_3 + 6H^+ + 6e = 2\ Al + 3H_2O$	- 1·49 - 0·059 pH
$Al(OH)_3 + 3H^+ + 3e = Al + 3H_2O$	- 1·47 - 0·059 pH
$Al\ O_2^- + 4H^+ + 3e = Al + 2H_2O$	- 1·36 - 0·079 pH
$H_2Al\ O_3^- + 4H^+ + 3e = Al + 3H_2O$	- 1·27 - 0·079 pH
$2\ Al^{3+} + 3H_2O = Al_2O_3 + 6H^+$	pH = 3·5
$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$	pH = 3·9
$Al(OH)_3 = AlO_2^- + H^+ + H_2O$	pH = 5·7
$Al_2O_3 + H_2O = 2AlO_2^- + 2H^+$	pH = 6·85
$Al_2O_3 + 3H_2O = 2H_2AlO_3^- + 2H^+$	pH = 11.4

The limits of reversible stability of water are defined by the following equilibria:

Reduction:

$H^+ + e = \frac{1}{2} H_2$ E = -0·059 pH

Oxidation:

$O_2 + 4H^+ + 4e = 2H_2O$ E = +1·23 - 0·059 pH

APPENDIX 2

THE GLOVE BOX

Key to Diagram of Glove Box, Figure 11.

A	Fibreglass box (Marine and Industrial Plastics).
B	Perspex front
C	Glove Ports
D	Evacuable Entry Port
E	Rotary Vacuum Pump
F	Flexible coupling
G	Vacuum gauge (20 to 0 mm. Hg.)
H	G.K.N. valve
J	Internal pressure gauge (- 2 to +2. ins. W.G.)
K	Speedivalves
L	Pressure switches
M	Magnetic valves
N	Circulating pump
P	Gas-sampling probe for moisture meter
Q	3-way tap
R	Tube containing molecular sieves
S	Steel frame
T	Argon supply
V	Excess gas pressure release through oil

All rigid piping in the glove-box gas circuit was $\frac{1}{2}$ inch copper, joined with Edwards high-vacuum O-ring seals: flexible connections for the argon supply were made by reinforced P.V.C. tubing.

The incoming gas was dried by passage through a packed bed of Molecular Sieve which was activated every fortnight; inside the box, gas was continuously passed through a small fluidised bed of molecular sieve which was renewed frequently. This not only dried the gas, but removed any fumes in the atmosphere. The glove box was operated under conditions where the moisture content of the argon was less than 10 ppm.; the moisture content was measured by a Shaw Moisture meter.

Apparatus was transferred to the box by way of the side entry port, which could be evacuated and back-filled with argon. Shoulder-length Veedip Neoprene gloves were used.

The gas-circuit included pressure-switches connected to magnetic valves so that the pressure of gas inside the box was automatically maintained at atmospheric pressure ±2 inches water-gauge.

The glove-box proved entirely satisfactory for the type of work described in this thesis; the main disadvantage of this type of box is its physical weakness and its inability to withstand large changes in pressure.

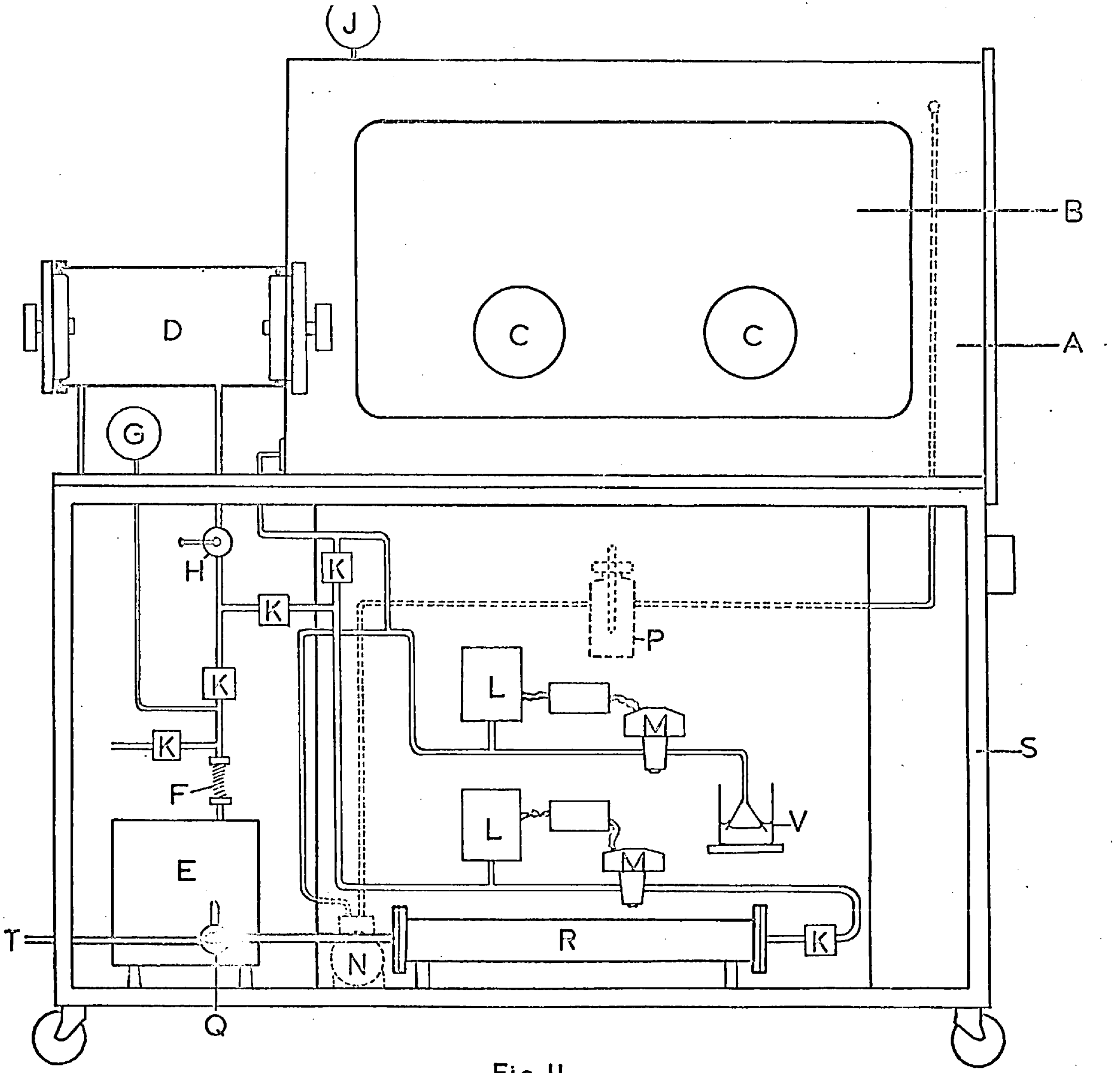


Fig. 11.

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Royal School of Mines

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