

Supported Homogeneous Catalysts

TRANSITION METAL COMPLEXES WITH POLYMERIC LIGANDS

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Almost all industrial catalysts are heterogeneous, the reaction taking place on a solid surface. During the past decade homogeneous catalysts, soluble in the liquid phase reactant, have received a great deal of attention, although they have so far found only limited industrial use, chiefly because of the difficulty of their separation from the reaction products. More recently an intermediate type, made by attaching the active metal complex to an insoluble polymer support, has been found to offer a promising new range of catalysts for the future. It is likely that a large proportion of these will be based on the platinum group metals.

A short review of catalysis by transition metal complexes with polymeric ligands contributed to this journal by Manassen in 1971 (1) had just three references. The 36 references of this article are an indication of the growth of interest during the past two years. A wide-ranging review, in French, of catalysis by all types of metal organic polymers covering the literature up to the middle of 1971 is the only other available survey of this topic (2).

Catalysts made by chemically bonding a transition metal complex to a polymer lie in between those usually classified as "heterogeneous" and those classified as "homogeneous". They are, like most polymers, insoluble in a solvent, and in this sense they are clearly heterogeneous. However, we have, for four reasons, chosen to call the systems "homogeneous". First, because these complexes with polymeric ligands are prepared from the usual "small" complexes that are used as homogeneous catalysts. Secondly, they are studied under comparable conditions to conventional homogeneous catalysts, for example at temperatures below 100°C.

Thirdly, they retain many of the ligands of the comparable "small" transition metal complexes and, fourthly, their chemistry can be most closely compared with homogeneous systems in that in the region around the metal atom it is to be expected that the interactions taking place are very similar to those for a complex that dissolves in the solution. But it should be recognised that others prefer to consider such catalysts as heterogeneous (3, 4). That these systems span both areas of catalysis is well recognised (1, 5).

Homogeneous versus Heterogeneous Catalysts

The relative merits of homogeneous and heterogeneous catalysts to the industrial chemist are well known and are only outlined here. Homogeneous catalysts have better defined active sites, usually have all of the metal atoms available as the catalyst, and the steric and electronic environment of the metal atom can be, at least in principle, varied very widely. The major disadvantage of the homogeneous catalysts is the need to separate off the reaction products and recover the

catalyst. This can be both complex and expensive. Other disadvantages are that these catalysts are relatively easily decomposed so temperatures must be well controlled, and that they can be deactivated if poisonous by-products are formed. Also corrosion of reactors by metal complexes is possible.

The advantages might be retained and the disadvantages removed if the homogeneous catalyst is either impregnated on to a solid support, or in some way chemically bonded to it.*

Preparation of Supported Transition Metal Complexes

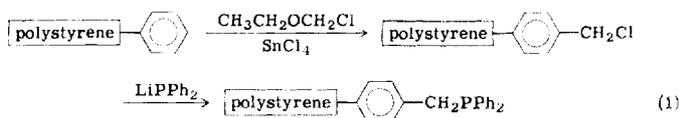
The first attempts were made by Bond and his colleagues in the laboratories of Johnson Matthey (7), and by Rony (8). Bond used rhodium trichloride in ethylene glycol impregnated on to Silocel as a packing for a g.l.c. column, and showed that pent-1-ene was isomerised to pent-2-ene isomers as it passed through the column. Rony studied the hydroformylation of propylene by $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ in butyl benzyl phthalate on granular silica gel. This reaction also takes place on this complex supported on carbon or alumina in the absence of the solvent (9).

The first attempts to bond the catalyst chemically to the support used ion-exchange resins with a variety of Group VIII metal complexes and the reactions studied included carbonylation, hydrogenation and hydroformylation (10). A detailed study of hydrogenation using K_2PdCl_4 on Amberlyst A27 resin has been published (11).

*An interesting alternative approach to separating catalysts and products without supporting the catalyst on a polymer has been reported by Parshall (6), who has used a molten salt (the tetralkylammonium salts of SnCl_3^- and GeCl_3^-) as the solvent. The organic products may then be easily separated by distillation. Using PtCl_2 in these molten salts, alkene hydrogenation, isomerisation, hydroformylation and carboalkoxylation have been studied.

Most workers have used complexes in which phosphine groups are used to link the metal to the solid support. Two types of polymer support, polystyrene and silica, have been most studied. With polystyrene the form of the polymer can be changed by changing the amount of cross-linking, a feature that appears to have important consequences on the type of catalyst produced. This is the type of support that has been most widely used. The polymer support based on silica has been developed by chemists at British Petroleum Co. Ltd., and the only work known to us so far is that reported by them (3, 12), and that carried out in our laboratory (13).

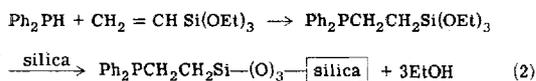
Polystyrene supports are most easily prepared by chloromethylation of a polystyrene cross-linked with divinylbenzene, and subsequent treatment with lithium diphenylphosphide (3, 14, 15, 16) (Equation



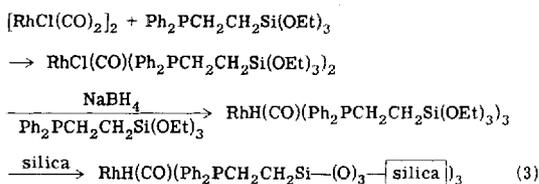
1), although the support has been prepared by polymerising *p*-diphenylphosphinostyrene (1). The transition metal complex with this phosphenated† polymer ligand is then prepared by equilibration of the polymer with a known complex in an inert solvent (17). Equilibration times and temperatures vary from two to four weeks at room temperature (14), to short periods under reflux.

Transition metal complexes with a silica ligand have been made by two routes (3). By one route the silica is first treated with (2-diphenylphosphinoethyl)triethoxysilane. This can be prepared by the addition of diphenylphosphine to vinyltriethoxysilane under ultra-violet irradiation (18) (Equation 2). The

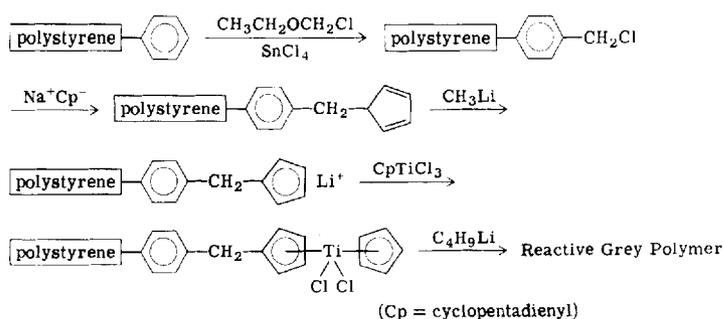
†Phosphenated will be used throughout to mean that the polymer has organophosphorus groups attached to it (e.g. in this case PPh_2 groups).



phosphenated silica is then equilibrated with a known complex, in a manner analogous to the polystyrene support above. The other route to the silica-supported complex involves the initial formation of a complex containing the (2-diphenylphosphinoethyl)triethoxysilane ligand, and condensation of this with the silica (Equation 3).



A range of metal complexes in which the polymer is either polyvinylalcohol (19, 20) or polybutadiene (21), or many other polymers (32), has been patented, although there are no reports of these complexes being used as catalysts. Also a polymer made by copolymerising an alkene containing phosphorus viz. $\text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2$, with styrene is claimed to give a viscous liquid that can be used as a catalyst support (22).



An interesting complex of titanocene attached to a polystyrene resin has been prepared (23) by the reaction sequence of equation 4 and it has been shown to be a very active catalyst (see later).

The Structure of the Catalyst

Detailed information about the structure of the complexes with polymeric ligands is difficult to obtain. Indeed, it is our belief that advancement of this area of chemistry could be seriously impeded by this very difficulty. Elemental analysis of the complexes gives the amount of the elements that are in the particular complex, but this information is of only limited value. Detailed information about the environment of the metal atom, what other ligands are present, and how they change when chemical reactions occur, is generally not known. For supported complexes prepared from carbonyl complexes, the C-O stretching vibration in the infra-red spectrum of a disc or mull can sometimes be detected (3, 24), and diffuse reflectance electronic spectra have been reported for both cobalt(II) and nickel(II) compounds (3).

In a study of rhodium and iridium complexes by Collman and his co-workers (24), the ligands present in the supported-complex were deduced by analysing the solution remaining after a phosphenated 2 per cent cross-linked polystyrene was equilibrated with a known rhodium or iridium complex. If the complex $\text{MCl}(\text{CO})(\text{PPh}_3)_2$ [M = Rh or

Ir] is used, both triphenylphosphine groups are displaced, and it can thus be deduced that the product is $\text{MCl}(\text{CO})\text{L}_2$ [M = Rh or Ir, L = phosphenated polystyrene] with two phosphorus atoms on the polystyrene forming

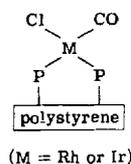


Fig. 1 Product $\text{MCl}(\text{CO})\text{L}_2$ [L = phosphenated polystyrene] of equilibrating a phosphenated 2 per cent cross-linked polystyrene with $\text{MCl}(\text{CO})(\text{PPh}_3)_2$ (24)

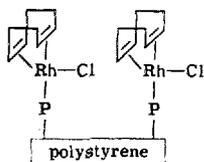


Fig. 2 Product of reaction of $[Rh(\text{cyclo-octadiene})Cl]_2$ with phosphinated polystyrene, as reported by Collman (24)

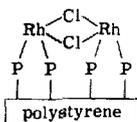


Fig. 3 Product of reaction of Fig. 2, using 2 per cent cross-linked polystyrene, as reported by Grubbs (23)

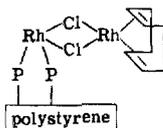


Fig. 4 Product of reaction of Fig. 2, using 20 per cent cross-linked polystyrene. Half the rhodium atoms will be bound as in Fig. 3 and half as here

a chelate ring to each metal atom, as in Fig. 1.

In this, and similar cases, it was not possible to form a complex by displacement of only one triphenylphosphine group, and it is suggested that the polymer chain is sufficiently mobile to bring nonadjacent sites together. Two triphenylphosphine groups per molecule of complex were also liberated when more highly cross-linked polystyrenes were studied. There appears to be some doubt about the product formed by the reaction of $[Rh(\text{cyclo-octadiene})Cl]_2$ with phosphinated polystyrene. Collman (24) reports the formation of the complex shown in Fig. 2, formed by splitting the chloro-bridges. In contrast, Grubbs and his co-workers (23) report that cyclooctadiene is liberated. If a 2 per cent cross-linked polystyrene is used (like Collman (24)), 2 moles of cyclooctadiene are liberated per mole of complex used, to form, presumably, the complex shown in Fig. 3, but if a 20 per cent cross-linked polystyrene is used only 1.4 moles of cyclooctadiene are liberated per mole of complex used. In this case half of the rhodium atoms will be bound as in Fig. 3, and half as in Fig. 4. These results would indicate, as might be expected, that in the 20 per cent cross-linked polystyrene there is less mobility of the polymer chains than in the 2 per cent cross-linked polymer.

Catalytic Reactions

A wide range of hydrocarbon reactions have been catalysed by these complexes with polymer ligands, viz. hydrogenation, hydrosilylation, hydroformylation, acetoxylation, polymerisation, and oligomerisation.

The published reactions are collected together in the table on pages 70 and 71 with the complex used in the preparation of the supported catalyst, the polymer used, and the organic molecules studied. The data given earlier by Manassen (1) are not included here, nor is the table totally comprehensive. For example, some patents tend to be wide ranging in their claims, and it is not possible to summarise them all in a small table.

Hydrogenation is a useful test reaction that has been widely used in homogeneous catalysis studies. Tris(triphenylphosphine)chlororhodium(I) has been much studied (33). With one of the triphenylphosphine ligands replaced by phosphinated polystyrene the activity of the complex as a hydrogenation catalyst is much more sensitive to the size of the alkene substrate. Whereas the rates of hydrogenation on $RhCl(PPh_3)_3$ of many alkenes are comparable, on the polymer supported catalyst the rate of hydrogenation of hexene is 6.25 times that of cyclooctene (14). This is attributed to restriction of movement of the solution within the cross-linked polymer, indicating that most of the reaction is taking place inside the polymer bead.

These lower rates of hydrogenation reported for cyclic alkenes compared with linear alkenes on a rhodium complex supported on polystyrene (14) are not found when a silica supported complex is used (13). Indeed, using a silica supported catalyst, cyclohexene is the most reactive alkene studied so far. Silica appears to have distinct advantages over polystyrene as the catalyst support, in that the rates of hydrogenation are higher. Using a catalyst formed by equilibrating $RhH(CO)(PPh_3)_3$ with phosphinated silica, the rate of hydrogenation of

pent-1-ene is six times that observed when the same complex is supported on phosphenated Amberlite XAD-2. A catalyst formed by reacting $\text{RhH}(\text{CO})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_3$ with silica is of comparable reactivity to the equilibrated silica-based catalyst. The reason for the higher activity of the silica supported catalysts is possibly that the rhodium complex molecules are on the outside of the silica particles, and therefore are more readily available to the reactants, than for the polystyrene supported catalysts where the rhodium complex may be deep inside the polymer beads. These supported complexes are still somewhat less reactive than related unsupported complexes in homogeneous solution. Grubbs et al. (34) report an activity of polystyrene-supported rhodium catalysts of 0.06 times that of an equivalent amount of the homogeneous counterpart, and the difference for the silica-supported catalysts will clearly be rather less.

Interesting differences occur in the pattern of the reaction with different complexes. For example, if $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is equilibrated with phosphenated silica, the catalyst formed is about half as active as a hydrogenation catalyst as that prepared from $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (13). However, the RhCl_3 -based catalyst is a very active isomerisation catalyst and almost all of the terminal alkene used in the reaction is converted to the internal isomer before it is hydrogenated. The reasons for these differences have yet to be explored. The efficacy of polystyrene supported rhodium complexes decreases as the following complexes are used for the equilibration with the phosphenated polystyrene: $\text{RhCl}_3 > \text{RhCl}_3 + \text{PPh}_3 > \text{RhCl}_3 + \text{PPh}_2 > \text{RhCl}_3 + \text{C}_2\text{H}_4 > \text{RhCl}(\text{PPh}_3)_3 > \text{RhCl}(\text{PPh}_2)_3$ (15). Catalysts using phosphenated polyvinylchloride as support do not appear to be very active (26).

Catalysts that selectively hydrogenate the polyunsaturated components of soybean oil without producing the saturated fats are of interest. Platinum and palladium chlorides

on a cross-linked polystyrene support give similar results to their homogeneous analogues; the products of hydrogenation of soybean methyl ester being the monoene and diene (27).

Activation of the catalyst by attachment to the polymer support is the most important feature of the work with titanocene (23). A necessary feature of a homogeneous catalyst is the existence of a free coordination site on the metal atom to which alkene molecules can attach themselves. Often attempts to produce a free site results in polymerisation of the complex and the free site is removed, but if the complex is bound to a rigid polymer there is the possibility that free sites can be produced. Titanocene is a reactive catalyst for alkene reduction, but it rapidly polymerises to an inactive compound (35). The catalyst produced by reduction of titanocene dichloride attached to polystyrene is six times as active as the analogous catalyst made from titanocene dichloride itself.

In addition to hydrogenation, hydroformylation is the other reaction that has, so far, been studied in some detail. During hydroformylation of a terminal alkene the aldehyde group can add to the end carbon atom giving a linear aldehyde, or to the internal carbon atom giving a branched aldehyde (see footnote to the table for description of hydroformylation). The amount of each aldehyde is dependent on the catalyst. For example when the catalyst is $\text{Rh}(\text{acac})(\text{CO})_2$ the ratio normal:branched is 1.2:1, and when the catalyst is $\text{Rh}(\text{acac})(\text{CO})\text{PPh}_3$ the ratio is 2.9:1 (3). If $\text{Rh}(\text{acac})(\text{CO})_2$ is equilibrated with a phosphenated polymer, either polystyrene, or polyvinylchloride, or silica, the catalysts obtained give a normal:branched aldehyde ratio in hydroformylation of 2.0-2.5:1, indicating, as would be expected, that they contain rhodium linked to phosphorus (3). The above change in aldehyde ratio on replacing a CO by a PPh_3 ligand is illuminated by the report that uses $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ as a hydroformylation catalyst and also the complexes prepared by attaching this

Reactions Catalysed by Polymer-supported Transition Metal Complexes			
Metal Complex	Polymer	Substrate	Reference
Hydrogenation (RhCl(C ₂ H ₄) ₂) ₂	poly- <i>p</i> -diphenylphosphinostyrene	—	25
RhCl(PPh ₃) ₃	phosphenated 2 per cent cross-linked polystyrene-divinylbenzene	cyclohexene hex-1-ene Δ ² -cholestene octadecene cyclooctene cyclododecene	14
RhCl ₃ RhCl ₃ then PPh ₃ RhCl ₃ then PPh ₂ RhCl ₃ then C ₂ H ₄ RhCl(PPh ₃) ₃ RhCl(PPh ₂) ₃	phosphenated 2 per cent cross-linked polystyrene-divinylbenzene	hept-1-ene crotonaldehyde vinyl acetate vinyl ethyl ether	15
K ₂ PdCl ₄	Amberlyst A27	cyclohexene styrene	11
[RhCl(COD)] ₂	phosphenated Amberlite XAD-2	hex-1-ene	3
NiCl ₂ then NaBH ₄ Rh(acac)(CO) ₂ [RhCl(COD)] ₂ RhCl ₃	phosphenated PVC	propylene hex-1-ene oct-1-ene	26
(EtO) ₃ SiCH ₂ CH ₂ PPh ₂	silica	hex-1-ene	3
[IrCl(COD)] ₂	phosphenated SiO ₂	hex-1-ene isoprene	12
PtCl ₂ PdCl ₂	phosphenated polystyrene -divinylbenzene	soybean methyl ester	27
titanocene	chloromethylated cross-linked polystyrene	cycloocta-1,3-diene cycloocta-1,5-diene styrene hex-3-yne hex-1-ene	23
RhH(CO)(PPh ₃) ₃	phosphenated SiO ₂ and phosphenated Amberlite XAD-2	pent-1-ene <i>trans</i> -pent-2-ene 2-Me-but-2-ene 2-Me-but-1-ene cyclohexene cyclooctene	13
RhCl ₃	phosphenated SiO ₂	pent-1-ene	13

Metal Complex	Polymer	Substrate	Reference
Hydroformylation			
Rh(acac)(CO) ₂	phosphenated Amberlite XAD-2 phosphenated PVC	hex-1-ene	3, 28
(EtO) ₃ SiCH ₂ CH ₂ PPh ₂	SiO ₂		
RhCl ₃ then C ₂ H ₄	phosphenated 20 per cent cross-linked polystyrene-divinylbenzene	hept-1-ene	15
[Rh(CO) ₂ Cl] ₂	cross-linked polystyrene -divinylbenzene substituted with —P(Ph) ₂ , —P(Bu) ₂ , —SH, —CH ₂ NMe ₂ , or —P(OMe) ₂	hex-1-ene	4
Hydrosilylation			
RhCl ₃ RhCl ₃ then C ₂ H ₄	phosphenated 20 per cent cross-linked polystyrene-divinylbenzene	(EtO) ₃ SiH and hex-1-ene or vinylethylether or acrylonitrile or trans-hept-2-ene	15, 29
H ₂ PtCl ₆ or RhCl ₃	cross-linked polystyrene -divinylbenzene substituted with —CH ₂ PPh ₂ , —CH ₂ NMe ₂ or —CH ₂ CN polymethacrylate with ester group —OC ₆ H ₄ PPh ₂ or —O(CH ₂) ₃ PPh ₂ or —O(CH ₂) ₂ NMe ₂ or —O(CH ₂) ₂ CN Amberlyst A21 allyl chloride-divinylbenzene copolymer with —CH ₂ PPh ₂ functional group	hex-1-ene hept-1-ene with HSi(OEt) ₃ or HSiEt ₃ or HSiCl ₃	30
Acetoxylation			
PdCl ₂	phosphenated silica	ethylene propylene isobutene	12
Polymerisation			
Ni(COD) ₂	phosphenated silica	butadiene	12
NiCl ₂	phosphenated polystyrene	ethyl propiolate	31
Oligomerisation			
NiCl ₂ then NaBH ₄	phosphenated PVC	phenylacetylene	3
NiCl ₂	phosphenated polystyrene	phenylacetylene	31
Me = methyl, Et = ethyl, Bu = butyl, Ph = phenyl, COD = cycloocta-1,5-diene, phosphenated — see text			
Hydrogenation: —CX=CX— + H ₂ → —CXH—CXH—			
Hydrosilylation: —CX=CX— + Si—H → —CX(Si≡)—CXH—			
Hydroformylation: —CX=CX— + CO + H ₂ → —CX(CHO)—CXH—			
Acetoxylation: —CX=CX— + CH ₃ COOH → —CX(O.CO.CH ₃)—CXH—			
Polymerisation and Oligomerisation: n(—CX=CX—) → —(CX—CX) _n —			

complex to polystyrene by a number of coordinating groups (see Table) (4). The ratio of linear and branched aldehydes formed from the terminal alkene is independent of the ligands on rhodium; however, the amount of isomerisation of terminal to internal alkene is very dependent on the ligands, being more for carbon monoxide and less for triphenylphosphine. The lower normal-branched ratio for the carbonyl complexes (3) can be explained in terms of these two competing reactions. Only branched aldehyde can be formed from the internal alkene that has been formed by isomerisation, and as more isomerisation occurs the linear to branched aldehyde ratio will fall.

Another feature of interest is that these hydroformylation catalysts with polystyrene ligands vary markedly in their efficiency as aldehyde hydrogenation catalysts, depending on the groups used to attach the rhodium to the polymer (4). Rhodium-phosphine polymer complexes are poor aldehyde hydrogenation catalysts, but rhodium-amine polymer complexes catalyse alcohol formation under very mild conditions. This is particularly interesting in view of the fact that the homogeneous counterparts of these amine complexes are far less active.

Complexes of cobalt carbonyls with polyvinylpyridine have been used to catalyse hydroformylation (36), but the catalyst in this case has been shown to be a solution of cobalt carbonyl that has dissociated from the polymer support.

Hydrosilylation is a reaction of some considerable interest and potential to the organosilicon industry. The usual homogeneous hydrosilylation catalyst is chloroplatinic acid, and its use necessitates the reaction being carried out in inconvenient alcoholic solvents to obtain a homogeneous reaction mixture. One group has reported the use of polymer supported catalysts (15, 29, 30). A whole range of functionally substituted alkenes can be hydrosilylated, the extent of the reaction decreasing as electron

withdrawing groups are substituted in the alkene (29). Unsupported chloroplatinic acid is a good hydrosilylation catalyst, and rhodium trichloride shows little activity. However, putting these two compounds on to polymer supports has a marked effect on their activity (30). Both complexes on all supports catalyse the addition of triethoxysilane to alkenes but differences in catalytic activity occur with triethylsilane and trichlorosilane. The complexes which are good catalysts for the addition of triethylsilane are less effective for trichlorosilane and vice versa. For some catalysts, such as the rhodium complexes with amino and cyano groups, there are no comparable soluble catalysts.

Conclusions

This review shows that research interest in transition metal complexes on a polymer support has increased rapidly during the past two years. The technological difficulties in using homogeneous catalysts have undoubtedly been the major factor in initiating this research. It is to be hoped that the advantages that homogeneous catalysts sometimes have to offer over their heterogeneous counterparts can be realised by putting the catalyst on a polymer support. As in all areas of research a number of interesting new facets of the chemistry these compounds have already become apparent. As the potential of these systems has only started to be explored, work will undoubtedly continue at an increasing rate. It is interesting to note that most of the compounds studied so far have been complexes of rhodium. It would seem likely that, as with most other types of catalysts, a large proportion of polymer supported catalysts will be based on the platinum group metals.

Acknowledgments

One of us (Z.M.) would like to thank the Chemistry Department at Hull University for its hospitality during the past year, and the British Council for its support.

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Weld Metal Temperature Measurement

HARPOON TECHNIQUE WITH RHODIUM-PLATINUM THERMOCOUPLES

The thermal history of weld metal gives a good indication of the behaviour of the weld thereafter. For example, the thermal behaviour of the weld bead affects the properties of transformable steel. To record the thermal history of a weld bead platinum metal thermocouples may be inserted during the welding process but until recently many of them melted in use and the instruments became open circuit.

C. Pedder of the Welding Institute's Metallurgical Department at Abington Hall, Cambridge, has now described a simple technique in which platinum: 13 per cent rhodium-platinum harpoon thermocouples of 0.5 mm wire arc used. The wires are insulated in twin bore ceramic insulators supported in a close-fitting steel tube so that they protrude 3 mm beyond the insulator, which itself protrudes 5 mm beyond the steel tube end. They dip into the pool of weld metal which completes the circuit by acting as the thermocouple hot junction. Tests showed similar results to those using con-

ventional thermocouples up to 1000°C. The e.m.f.s differed by less than 0.01 mV (10°C at 1000°C).

Manual and semi-automatic methods have been used to plunge the thermocouple accurately into the weld metal pool. In the latter case the welder can also operate the harpoon thermocouple, and when used with implant cracking test equipment the thermocouple records the thermal cycle and also actuates the implant loading mechanism at the predetermined temperature.

Weld thermal cycles and cooling times have been measured by the harpoon thermocouple for the MMA, MIG and submerged arc processes. It has also made possible the thermal analysis of weld metal austenite transformation immediately after deposition, whereas previous dilatometry studies gave transformation characteristics of reheated metal. The thermal analysis process uses a differential amplifier to convert thermocouple output to a voltage proportional to the cooling rate.

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