THE CHROMISING PROCESS: A NOVEL DEVELOPMENT

by

C. C. HANSON, C.ENG., FIM

Thesis submitted in fulfilment of the regulations
for the degree of Master of Philosophy
at Loughborough University

August 2002

Supervisor: Prof. D. R. Gabe

Institute of Polymer Technology and Materials Engineering
Loughborough University

ACKNOWLEDGEMENTS

I wish to thank my friends at Joh. Winklhofer and Söhne GmbH & co in Munich for the co-operation and encouragement given during this project.

Special thanks go to Herr Sessner, Head of the Laboratory for his continued support through some difficult periods and also the many critical discussions we had.

In addition, I wish to thank Herr Girg, Technical Director, whose enthusiasm for and ultimate confidence in the project was most important to me.

Some physical methods were carried out on site but others were made at Cambridge and Loughborough Universities in addition to work carried out on a contract basis at several laboratories in Germany. All of this help has been much appreciated.

Because of how the project evolved, photographs suitable for inclusion in the text were not always available and recourse has been made to drawings and sketches where necessary.

I also wish to thank Professor D.R. Gabe, my academic supervisor for his help during the preparation of this thesis and for arranging the work done at Loughborough.

Finally, I am deeply indebted to Dawn Butler in preparing the work for submission and publication.

SYNOPSIS

The industrial application of the chromising process started in about 1935. It enjoyed a steady growth until about 1975 but has since declined in importance, being replaced by novel C.V.D and P.V.D processes. Its use for corrosion and oxidisation resistance is very small but there are some applications for wear resistance which exploit the high hardness of chromium carbide.

A chance observation in the wear pattern and performance of chromised automotive timing chain link-pins, led to the identification of a diffusion coating structure which had not been previously recognised as having enhanced wear resistance. It was the purpose of this research to examine the nature of this novel structure, to determine how it was occurring in practice and to develop a chromising process which could consistently reproduce the desired end product.

The literature on chromising, with particular reference to hard coatings, has been reviewed, as was the range of process methods which have been used in the past, but which have been discarded for one or more reasons.

Examination of the mechanics of these processes, when related to the quite small pin components involved, and the structural requirements of the coating, led to the adoption and development of a dynamic as opposed to the more common static process. Although there was some industrial know-how, because there is no published data, the various parameters of the process had to be determined and standardised. This involved plant development as well as that of the processing powder.

The outcome of the research programme was ultimately successful, with steady-state production of the special chromised coating giving a superior performance and this has been confirmed commercially with increasing product output. However, the correlation of the modest amount of previously published literature with the results of this work, has so far proved difficult.

CONTENTS

1. **INTRODUCTION**

2. **THE CHROMISING PROCESS**

3. **EXAMINATION OF CHAIN PINS FROM SERVICE**

4. **THE DEVELOPMENT OF THE NEW PROCESS**

5. **FURTHER DEVELOPMENTS**

6. **DISCUSSION**

APPENDIX

TABLES

Table I Composition of three chromised coatings as obtained by E.P.M.A.

Table II Composition range of powders in use both before and after regeneration [taken from routine analysis results].

Table III Results of fractographs made prior to X-Ray diffraction analysis.

Table IV Examples of analysis results of coatings obtained by E.P.M.A.

FIGURES

1 INTRODUCTION

1.1 Historical Background

Roller-type transmission chains either the single or double-ganged type have been widely used as the timing chain in internal combustion (i/c) engines for many years. Development has been of a steadily progressive nature with modest improvements rather than sudden major advances. In fact, perhaps the most significant development has been the toothed rubber belt which is hardly metallurgical. Therefore it was surprising for a motorcar manufacturer to claim that some chains of nominally the same specification and manufacturing route should perform much better than others when operated under similar conditions.

Obviously, if the claims were substantiated then, with the constant pressure to achieve improvements in the cost/performance of i/c engines, this was something which must be investigated. Accordingly the motorcar manufacturers approached one of its German chain suppliers, Joh. Winklhofer of Munich, with what information it had gathered and the request they look into the matter.

Fortuitously, the author was at the time of the technical meeting acting in a consultative capacity for Joh. Winklhofer and was asked to investigate the problem.

The industry standard, at the time, was for the link pins to be chromised, which gave improved performance when compared with carbo-nitrided pins. The chromised layer was a mix of carbides of chromium and iron but was accepted as being essentially a single layer. The observations of the motorcar manufacturer however, suggested a two or even three layer coating with the outer layer considered quite significant in reducing wear. Thus the problem was to determine the constitution of the novel chromised layer and whether it could be reproduced commercially.

In accordance with normal practice in the automotive industry, supplies of a given component are sourced from more than one supplier and in this case it is likely that three suppliers were involved, one German, one French and one Japanese. Although the specification of the chains bought from each supplier was nominally the same, particularly with regard to dimensions and mechanical properties, there was some latitude allowed in how the performance of the component was achieved. Test programmes were developed between purchaser and supplier, data established as to minimum performance requirements and these incorporated into the final purchase specification.

It was common knowledge within the industry, that the three suppliers were offering chains in which the pin was chromised, and there was also some knowledge as to how the three suppliers were carrying out the process, but obviously not its detailed production specifications. There was an assurance from the motorcar manufacturer that to the best of their knowledge, all dimensional and material aspects of the different chains were within specification. Thus it seemed fairly certain that the varying performances were being caused by a function of the chromised coating hence the need for an investigation and development programme.

1.2 Objectives

The objectives of this work are essentially threefold.

A. First, a comparison must be made between the chromised pins of the so-called normal chains and those found to give a longer life and why this should be.

B. Second, to develop a process or modify an existing one which consistently reproduces the better coating.

C. Third, to confirm that the developed coating fulfils the expectations shown by the observations in service of certain chains which were made by the motorcar manufacturer.

2 THE CHROMISING PROCESS

2.1 Literature and Historical Review

The process of diffusion of chromium into steel and certain other substrates such as nickel has been reviewed from time to time over the past sixty years,(2, 3, 4) but the recent review by Castle and Gabe(1) has been much needed by bringing together the fairly substantial amount of work carried out over the past forty years. They cite about 200 references covering practical processes, the theory of chromising, (particularly its thermodynamics) and the characteristics of chromised coatings.

In the context of the current work, the term 'chromising' implies a process in which a ferrous-based component is surrounded by a chromium rich 'atmosphere' at an elevated temperature during which some chromium is absorbed by the substrate of which the compound is made. It is recognised that it is possible to electro-deposit chromium onto the surface of ferrous based components as an 'overlay coating' and to effect some diffusion and alloying by heating the component in an atmosphere of dry hydrogen, but that technique is not under consideration.

F.C. Kelley, an American working at the US Bureau of Mines, is generally given the credit for the invention of chromising with his U.S. Patent 1,365,499 (1921). It is noted that Castle and Gabe(1) seem to give the honour to H.C.P. Weber with a first patent 1,373,038 (1919), but it should be noted that numerically Kelley's is the earlier application but which may have met some problems in the search procedure.

Suffice it to say that while Weber seemed to slip from the scene, Kelley continued working in the field with other patents and eventually joined the Research Laboratory at General Electric Company, Schenectady. He was still active in 1948, contributing the section on Chromium Impregnation or 'chromising' in the Metals Handbook published by the American Society for Metals in that year. Sadly, even thirty years after his original work he still gave the primary method of chromising as packing the low carbon steel part in a mixture of 45% alumina and 55% chromium (by weight), and heating in dry hydrogen at 1300-1400°C for 3-4 hours. This is done in a laboratory tube furnace which shows how little he had moved forward either experimentally or, more importantly, industrially or commercially. Anyone who has carried out this method will know how disastrous the results are because of the sintering of the chromium onto the steel surface. To be fair, in his article, he does refer to the classic paper of 1941 by Becker, Daeves and Steinberg(5), who were employed by Deutsche Edelstahlwerke, of Krefeld, Germany and who, in the mid 1930s developed the first workable chromising process.

However, they were preceded by L.H. Marshall who, with his U.S. Patent 1,853,369 of 1927, introduced the use of a halide into the process, and made it much easier in pursuit of an industrial process.

When one realises that, in 1901, Sherard Cowper-Coles first patented 'Sherardising', that is the direct heating of ferrous substrates in zinc powder to obtain a diffused layer of zinc in iron, it is not a big leap to look at the same idea in relation to other combinations of metals and non-metals. Indeed, the impregnation of carbon into iron seems to have been known in antiquity but it was not until the classic work of Sorby at Sheffield in the latter half of the 19th century, that one was able to start an understanding of the physical chemistry involved.

Another researcher, who carried out much work in Paris in the 1920s, was L. Laissus. His work was published in Comptes Rendus and Revue Metallurgique of which Ref.(6) is a good example of early chromising. In fact, Laissus seems to have tried to diffuse both metallic and non-metallic elements into a range of substrates.

However, it was the German group at Deutsche Edelstahlwerke(5) who put together the first viable industrial process for chromising. This has been described in many papers and is generally termed the B.D.S. process after its three collaborators. Work was started in the early 1930s for one of two possible reasons. Firstly, Germany under Hitler was re-arming and chromising looked to be a possible way of conserving chromium and secondly D.E.W. wanted to move into the stainless steel market. It was probably a combination of both. D.E.W. took out both German and British Patents(7) before the 1939-45 War and, during the war, several companies in Germany carried out chromising processes(8). The only company in the U.K. to become involved in chromising over this period, was the Scottish steel company, Colvilles Ltd of Glasgow, who took out a licence from D.E.W. and set up a plant at Belshill, Lanarkshire, with the name 'The Metal Gas Co. Ltd'. R.L. Samuel was employed by this company for a time and he was also a member of the British Intelligence Objectives Sub-committee team which toured Germany in 1945-46 gleaning as much information as it could on the war-time chromising operations. Additionally, under the Custodian of Enemy Property Act, all pre-war and wartime developments in

Germany, including patents (German, U.K. and U.S.A. etc.) were declared public property and free to be used by anyone. This situation led to the establishment of nominally new processes and patents.

At this point in the 'discussion' it is worthwhile to consider some of the practical aspects of chromising, because they were responsible for the wartime and immediate post war developments in the U.K. A fundamental problem with any coating process, on both metallic and non-metallic based components, is how to support that component, so that it is 100% coated free from blemishes. For example, in electroplating there are witness marks where the part is wired or clipped onto a suitable jig. These marks are kept to a minimum by subtleties of design, or if that is not possible, they are accepted. In the glazing of ceramics, the item is placed on a small refractory (usually) three point support in the kiln, but this leaves the characteristic indentations on the base. In the high temperature processes applied to ferrous-based components, one has the added complication of distortion, either from the relieving of stresses or, simply the sagging of the part under 'its own weight' if not properly supported. Even supporting has its own problems which can result in contact marks, local welding, and, in gaseous/liquid processes, an interference with the flow of the active medium in the area of the support. As a result the desired coating will be thinner at these points and, where one is trying to achieve either corrosion or oxidation resistance, a weakness in the degree of protection. All of these factors are well enough known by technologists working in these areas of manufacture. Chromising is no exception and working with simple mild and carbon steels, their mechanical strength at the normal chromising temperatures is quite low, hence the distortion problem.

The theoretical basis at the back of the B.D.S. process was to use chromous chloride ($CrCl_2$) as the sole chromising agent. This required a two-stage approach during the first stage of which, the $CrCl_2$ was generated by the high temperature action of HCl gas on a low-carbon high-chromium ferrochrome (one could use pure chromium) in the presence of porous ceramic chips. On cooling down, the $CrCl_2$ condensed onto and into the ceramic chips. These chips were then used in the second stage of the process as the source of chromium **and** they also gave good support to the steel components placed therein. However, following a logical approach, and recognising the need for the $CrCl_2$ vapour to freely percolate through the operative mass, the refractory chips were relatively large (12-24mm) and this could be a limiting factor on the size of components processed. Also, the parts and ceramic charged with $CrCl_2$ had to be placed in a sealed retort and $CrCl_2$ is an unpleasant substance to have to handle, being very hygroscopic and injurious to health. As a process, it was labour intensive and lengthy because of its two stages. It persisted for a year or so but then it was modified, so that ferrochrome chips (3-5mm) were added to the refractory thereby effecting regeneration with $CrCl_2$ in situ and converting it into a single stage process. But another problem now arose, namely the sintering onto the steel component surface of the ferrochrome chips. These could be dislodged or knocked off, but could (did) leave a blemish and weakness in the chromium-rich coating. This was the process that found its way into Scotland at The Metal Gas Co. Ltd just before the war (1939) and it is what R.L. Samuel saw. It is also very probably the total extent of factory chromising being carried out in the industrialised world at that time, irrespective of the scientific papers emanating from the U.S. and France.

R.L. Samuel was himself French and trained there as a chemist just before the war. He was one of three brothers, all of whom eventually became involved with chromising. As a result of what he had seen and experienced at The Metal Gas Co. Ltd, he had the idea of using much finer powder and of generating the chromium halide in situ by using the ammonium salt of the halide, but he needed a backing organisation.

A company, Diffusion Alloys Ltd was set up with laboratories at London Bridge, the head office of a trading business and because the war was still ongoing the whole operation was under the control of The Ministry of Supply and secrecy was imposed. Finance also came from the old Ministry of Supply by way of research contracts. There were no industrial developments/applications until about 1950, when the company was allowed to operate freely. Various patents were taken out worldwide with licences in the U.S. forming The Chromalloy Corporation and in France the company S.A.P.D.A.L. of Paris (Société Anonymé Pour la Diffusion des Alliages). Also published at this time were the series of papers or articles by Samuel and Lockington(4) which opened up the whole concept of chromising and its industrial applications, and led to other workers carrying out research.

However, G. Samuel, one of the brothers mentioned previously, quarrelled with the others and went to the U.S. and set up Alloy Surfaces Ltd. Thus, together with a second licensee of Diffusion Alloys Ltd based in California, there were three companies offering a similar service in the U.S.

Over this period of 1950-1960 one sees a fair amount of 'house' literature, i.e. bulletins and one page articles in such magazines as Iron Age(9, 10, 11) describing the successes in application of chromising but sadly, while each was strictly true, they did not develop into major sources of revenue, and the companies had a difficult time and only just survived. Their survival was in fact due not to any advance in chromising technology, but in the application of the techniques of chromising i.e. the fine grain pack process, into the field of aluminising of gas turbine nozzle-guide vanes. Two companies, Chromalloy and the Californian unit, joined forces and, via Pratt and Whitney and Boeing, became the largest practitioner of gas turbine coatings and hardware repair. Alloy Surfaces got involved with the Lee-Wilson open-coil annealing process together with Inland Steel, to try and develop coil chromising(12). This was also tried by The Bethlehem Steel Co.(13) with much more success, but again, neither of these techniques has survived. There were some difficult practical problems with distortion of the open coil and eventually, the economics of competitive materials caused the coil chromising route to be abandoned. Today, except perhaps in the area which is the subject of this project, there is little, if any, pack chromising applied to low carbon, low alloy steels in the U.S.A.

Meanwhile in France, the company S.A.P.D.A.L. had been in discussion with a French cycle chain manufacturer S.E.D.I.S. with regard to the application of powder methods of chromising for use on the chain-link pins. Also, at what had now (1955) become The Chrome Alloying Co. Ltd, R.L. Samuel and H. Dorner were carrying out experiments with what was to be termed 'barrel chromising'. It was a crude affair, but at least established that it was possible to effect chromising when parts and powder were moving relatively to each other. Up until this time, all processes had been static. The results of this work were passed to the S.E.D.I.S company in France, who took out a licence via S.A.P.D.A.L. to use the process for the processing of roller chain pins, which, with development, is still in use today. Pins so processed were not widely used at first, with the 'deluxe' chain being termed the DELTA chain (perhaps from the word diffusion), but today substantial lengths of chain have chromised pins. S.A.P.D.A.L. as a company, ceased to function in about 1968-70 and to the best of current knowledge, there is now no other chromising activity in France except perhaps by Renold Chain Co. in Calais.

In Germany, there was no chromising immediately after the war, but D.E.W., in about 1949, recommenced activities because of a requirement for chromised bolts for the track of the re-built Railway Network. This facility was set up at a furnace builder, Grünwald, near Hilchenbach in Sauerland. The advantage was in being near the bolt makers. Here again, although there were one or two special items processed, the set-up as a whole, was geared to the nuts and bolts for the railway. The process containers were about 1½ metres outside diameter and were of doughnut shape to obtain a good, even, heat distribution. The hydrogen atmosphere was circulated and HCl gas was admitted at about 900°C. The bolts were again packed in ferrochrome chips as mentioned earlier and coatings of 100µm were obtained. Inspection was by immersion in dilute HNO_3 overnight to check for gas evolution. Visual inspection was accompanied by physical removal of any sintered-on particles. D.E.W. did some useful steel development to obtain good solid-solution coatings low in carbides by introducing titanium and or niobium into the steel and also copper and/or nickel to give the potential for precipitation hardening. Again, this plant no longer exists.

The activity of S.E.D.I.S in France regarding the chain pins caused interest in Germany, Italy, U.K., U.S. and Japan. In Germany, the idea was taken up by Winklhofer of Munich who developed a modified process but this will be discussed in more detail later. In Italy, 1975, Regina Chain co. of Milan made trials with pack chromised pins but did not pursue the matter. In the U.K. Renold Chain of Manchester worked with Diffusion Alloys on a very sophisticated coating application for sprag-type clutches, again using pack techniques and then went away and adapted what they had learned to extend the practice to chain pins. In the U.S. Morse Chain, a division of Borg Warner (through their U.K. unit at Letchworth) had considerable quantities of pins processed by Diffusion Alloys but with the closure of the Letchworth facility, this work ceased. It is not known what is happening in the U.S. at present but certainly some know-how exists there. In Japan, there is active chromising of chain pins, particularly by Daido. This company in its early days in chromising, combed the world for information and had no qualms about using patented process data. To cover themselves, they applied for and were granted spurious patents, but in practice used the previously proven systems and it was virtually impossible to prove that the original route was and still is used. There have been some technical exchange visits between these different chain manufacturers, so it is known what basic processes are at present in use.

Something ought to be said about the Russian and Chinese activity in the field of chromising. The Russians have been active in metallic diffusion since the end of the 1939-45 War, but this activity had been substantially influenced by the political situation. They were not signatories to the Geneva Patent Convention and therefore were free to plagiarise any Western ideas. It was possible to obtain a Russian Patent but it was a laborious process and had to be applied for at the same time as a U.K. Patent - one was not allowed the period of grace of the Western system. They had two laboratories involved in diffusion coating one of which was under Gorbunov(14) and the other under Minkevich(15).

There was animosity between these two groups as shown by the way in which they criticised each other's work. Further the work itself was very turgid with a short set of experiments and then reams of abstruse mathematical analysis, most of no useful purpose. Additionally, they had no compunction at taking someone else's results, packing an elementary laboratory scenario around them, and passing them off as their own work. They would also do the same with a patent, pre-date it and therefore give Russia the full use of it on the basis of 'prior art'.

The picture in China, as one would expect, has been similar to that in Russia, but here, until recently, they have taken ideas, plant processes etc. and if there has been any advantage to them, have blatantly copied. It was here that, in 1983, the writer saw salt bath chromising incorporated into a production line and claimed as their own invention.

Before completing this section on what is a simple historical account of chromising, some comment is warranted upon the relatively large amount of publications dealing with the physical chemistry of chromising. They seem to outweigh those on the practical aspects certainly as exemplified in the review by Castle and Gabe(1) and also in Powell *et al*(16) albeit on an earlier occasion (1966). It probably goes without question to say that the thermodynamic work has all been carried out on relatively small laboratory scale equipment - it is the way things are done. However, when one is dealing with even a 200kg charge at 1000°C, let alone a pack size of 2,500kg, consideration of the data produced by thermodynamics becomes difficult to apply. The writer has been directly involved with the chromising and other C.V.D. processes in the U.K., France, Holland, Belgium, Italy, Germany, Israel and the U.S. for the past forty-five years or so and with all the metallurgists involved yet the terms 'free energy' 'Fick's Law' etc. were hardly ever heard. So much of the work was done empirically, trial and error, often working on the basis of intuition. Perhaps a lot of industrial activity is like that; when something works, establish the parameters, keep to them and get on with the next job.

For chromising, it is perhaps rather sad, that, after eighty years since it was first proposed and more so after the considerable activity since the Second World War, today it finds itself used for producing hard coatings on chain pins and for the protection of hot section hardware in gas turbines. The former is carried out in France, Germany and Japan and the latter in the U.S. and the U.K. However, it is probably true to say that all of these applications owe their origin [as processes] to the original R.L. Samuel patents with Diffusion Alloys Ltd, U.K.

2.2 The practical techniques available

Some techniques have already been mentioned earlier and will now be discussed in detail. One however, namely salt bath chromising or its near neighbour, 'metalliding' is only mentioned for completeness because it is quite unsuitable for the purpose of processing the small chain pins, the subject of this research.

The first practical process was the B.D.S process devised by Becker, Daeves and Steinberg(5) but, as previously noted, this was modified in the light of industrial usage. As shown in Fig. 1, the unit consists of a bell furnace of somewhat squat form which sits over an inner container, the bottom edge of which, lies in a sand seal. Inside, this inner container are placed smaller containers, which hold the parts to be chromised plus the chromising medium. The arrangement is similar to that found in a pottery kiln.

Alternatively, the inner container may be of the full diameter with a central hole in the manner of a doughnut, with a slice taken off horizontally, thereby allowing access to the interior. The parts and medium are packed in the annular space. Up through the hearth of the furnace and into the inner container, there is a tube through which can be passed various gases as required.

The powder is coarse, consisting of a substantial percentage (75-80% by weight) of 70/30 ferrochrome with a refractory diluent alumina. The containers are filled on a layer-by-layer basis, with the parts sprinkled or placed on each layer of media, until the container is full. There is no solid halide added but there is residual chromous chloride on the media from the previous process cycle. The containers are placed on the hearth and the inner bell lowered into position.

The furnace is switched on and the inner bell purged with nitrogen to get rid of as much oxygen as possible. At a safe period later, hydrogen is admitted or a nitrogen/hydrogen mixture. This 'mops up' any residual oxygen, but there is very little of this at temperatures above 600°C, because of the large surface area of chromium rich metal available. At a temperature of about 800°C, a quantity of HCl gas is bled in on a hydrogen carrier. This activates the chromising reactions, supplementing the chromous chloride already present and ensuring some residual chromous chloride when the furnace has cooled down at the end of the process cycle. This is typically 24 hours with a maximum temperature of 1020°C.

The last unit seen operating in Germany about twenty-five years ago consisted of two hearths with one bell furnace. This allowed for a steady state throughput. Obviously, care must be exercised throughout the whole process cycle because of the risk of explosion. This required the maintenance of a positive pressure within the inner bell at all times (not less than 12mm H_2O with a deep, fine sand, seal). However, the flow-though rate must not be so high as to seriously dilute the chromous chloride component.

When cold, the inner bell is lifted off and the containers emptied onto a rubber coated vibrating grid which allows separation of parts from 'powder'. The parts are thoroughly washed to remove condensed chloride phases, dried and inspected to remove any adhering particles of ferrochrome. They are then steeped overnight in dilute nitric acid (about 10% by volume) to check for any coating discontinuities made visible by gas bubbles. Any parts so found will be reprocessed. After washing, the parts are dipped in aqueous sodium hydroxide to neutralise any remaining acid, washed, dried and packed. Direct experience of this process showed it to be very effective for the processing of engineering components such as nuts and bolts and other fasteners of reasonable dimensions. However, it was not suitable for sheet components because of the coarseness of the chromising medium.

The second practical process was the D.A.L. process devised by R.L. Samuel(4). As has already been stated earlier, Samuel had a detailed working knowledge of the B.D.S. process and it was the perceived problems of that process which led him to experiment with other halides and refractory diluents and, of equal importance, to examine methods of reducing costs by changing the chromising containers and the furnace practice.

Discussing the powder or compound first, it was recognised that the coarse B.D.S. medium did not offer good support to a wide range of components when heated to the 1000°C or so required for chromising. But it did give a good gas circulation around the parts. Samuel's approach was to use a fine ferrochrome powder (about 70 mesh) with a fine refractory diluent, such as kaolinite. This restricted the movement of the active gases, but supported the components better and the fine ferrochrome provided a much larger surface area for reaction with the halide gas. In addition, experience with the use of chlorine as the reactant halide showed that the powder became damp over a modest period of non-use due to the hygroscopic nature of the ferrous and chromous chlorides which condensed onto the refractory and ferrochrome particles. While the metal chlorides are not pleasant to handle on an industrial scale, the fluorides and bromides are worse, particularly the latter. This left iodine for consideration and although its cost as ammonium iodide is much higher than that of ammonium chloride, it was found that the powder remained much more dry than when using the chloride. Further comment will be made on related aspects in 2.4.

The containers or 'retorts' used with the D.A.L. process were designed with muffle furnaces in mind and the classic types are shown in Fig 2. They consist of a 'box and lid' or a 'cover and tray' system. As with the B.D.S. process, the parts and powder are built up layer-by-layer to within about 75-100mm of the top and the final covering is a layer of old powder. Sometimes a steel plate is placed on top, which is luted in with a fire clay paste. To seal the retort, powdered glass is put in the trough or channel and the lid or cover put in place and bedded down. With a furnace charger or adapted forklift truck the retort is placed directly into a muffle or bell-type furnace already at the required processing temperature and the retort is allowed to heat naturally. The powdered glass in the trough, being somewhat exposed, melts before the retort is up to temperature so forming a liquid seal. The expanding gases within the retort mass simply bubble out through the viscous glass until stability is reached. On completion of the process cycle, the hot retort is removed and put to cool down naturally. The lower pressure which develops in the retort will suck upwards some of the now solidifying glass until a stability is achieved. When cold, the retort is opened, any inner protective plate and fireclay removed together with any heavily oxidised compound if present, hence the use of old or 'spent' compound on top of the packed retort. The powder may then be removed with vacuum suction or the retort up-ended onto a shaker/sieve unit to separate out the processed parts.

The compound or powder of the D.A.L. process is much more 'dusty' than that of the B.D.S. which is a disadvantage in the final cleaning. For this operation, brushing and tumbling are used and this can be of considerable importance when solid solution coatings are involved because of sintering of ferrochrome particles onto the surface of the component. It is of less significance with carbide coatings. Although there may be residual chromium and iron iodide condensed phases on the coated components, they are less hygroscopic than the respective chlorides and water washing etc. has never been considered necessary to remove them. Nonetheless, work was always dipped into a dewatering oil (Ensis™ made by Shell Chemicals), which contained corrosion inhibitors.

Before completing this section and recognising that the technique had been previously declared unsuitable for processing chain pins, some mention should be made of salt-bath chromising and its subsequent derivative, fluidised bed chromising. Salt bath chromising is not new being more than fifty years old, and was an obvious development from the B.D.S. process. However, it did not achieve any significant industrial application because the best applications for it had not become fashionable. These were in fact press tools and the like used for metal forming.

Molten salt processes have an inherent problem, namely the removal of the salt. In very many applications in the ferrous engineering industry, the molten salt covered component is transferred to an oil or water quenching tank thereby achieving the desired hardening. It may involve a two-stage salt bath unit to ensure the optimum quenching temperature. Whichever route is followed, the end result is that the molten salt is blown off on quenching and disperses in the quenching medium. Compressed air has been used with limited success. Otherwise the salt covered component is allowed to cool to room temperature and then placed in hot water to dissolve the salt. This is a laborious business and corrosion can result.

In the 1970s with the hard coating of press and die steel tools becoming more significant (hard chrome plating had been available for many years), the Japanese car company, Toyota, brought out the TD process for chromising tools(17). This was a salt bath process based upon borax and chlorides in which the chromising potential was maintained by feeding in chromium metal powder. It was operated at 900-1050°C which is the quenching temperature range for many conventional tool steels such as D2 and others in the H group. It is difficult to assess how popular this process has been because it has been largely superseded by the TiC and $TiCN$ C.V.D. and P.V.D. processes.

A variant of the TD process, which it is worth mentioning but which is still not fully relevant to the present work, is T.R.D. or thermal reactive deposition. This uses a fluidised bed technology based upon alumina balls mixed with either pure chromium or ferrochrome. The activator or transfer agent (powdered NH_4Cl) is fed in with the argon fluidising gas. This technique overcomes the molten salt problems of the TD process. It gives satisfactory coatings and is still the subject of industrial and academic research(18).

2.3 Some further observations on the Practical Techniques

There is in all thermal processes as applied to metal products, the problem of thermal gradients, both within the product itself, and within the processing medium or the container. The process of chromising is no exception and, in fact, difficulties are considerably greater than with simple annealing and hardening, because fairly complex chemical reactions are also taking place. As is well known, temperature has a very marked effect upon the rate at which the reactions occur and, what is equally significant, upon what reactions take place. Time is also of fundamental importance, and therefore, it is pertinent that these two purely physical factors are examined in relation to the processes described in 2.2.

In the development of a new process in the metallurgical industry, there appears to be an initial flurry of activity with the publication of papers and literature, followed by a period of searching for likely applications to pay for the original costs and to sustain further development. Many samples are produced but only a few come to fruition, and it is at this stage, when continuous production seems assured, that the process equipment is developed to suit its economic application. Very often, the process is applied on a sub-contract or jobbing basis, such that the equipment developed has to be more multi-purpose than one would normally choose. Indeed, one is fortunate if there is an application found, which requires the setting up of a plant dedicated to one type of product, and in this case the customer often chooses to operate the process under licence. This has been the case with chromising and other processes, which come under the general heading of 'pack-cementation'.

The term 'pack' implies a powder-like substance, which may be coarse (granular) or fine (powder), or even a mixture of both. The constituents are part metallic and part non-metallic i.e. refractory. Although the metallic component may, in its massive state, have a good thermal conductivity, as granules or powder, this property is markedly reduced, and refractories are of very low thermal conductivity. Therefore, collectively, the pack-cementation powders are naturally low in thermal conductivity, and, in a thermal process, this imposes problems.

In Fig. 2 is shown a conventional chromising retort as used in the D.A.L. process. Its size can vary from 300x300x600mm to 300x600x1000mm. The largest ever used was 1000x800x6000mm. Whatever the size, there will develop thermal gradients within the powder and the steel components being processed. In fact, the 'solid' steel components improve the overall thermal conductivity of the 'pack' or retort. In the larger retorts it is possible to have a thermal gradient in excess of 10°C/mm such that the outer surfaces of the metal retort are well above visible red while the centre of the mass is still at about 100°C. The effect of this can be quite troublesome and has imposed limitations of application, particularly with regard to size of component processed. For example, in processing sheet or tube, one dimension of the retort must be kept as low as possible to improve the heating through of the mass. This imposes in its turn an economic penalty.

In Fig 3 is shown a horizontal section through a flat, rectangular or square box/retort. In Fig 3(a) it can be seen how the corner unit A receives heat on two faces while B and C only receive on one face and D by conduction from B and C. The possible isothermals are shown in Fig 3(b). The sequence of events on heating a retort of this type is likely to be as follows: -

1. A will heat up quicker and reach the chromising temperature first followed by B, C and D.
2. As D approaches temperature so any gas (air) and moisture will expand and force its way through A, B and C with the possibility of interfering with the gas composition in those areas and thereby altering the chromising characteristics or affecting the coating which has already been formed. This is of particular significance when forming carbide coatings because of the decarburising potential of oxygen and water vapour.
3. Because A will be at chromising temperature longer than D (even allowing for cooling down in air after removal from the furnace), components in A will have a thicker coating than in D but also its constitution is likely to be different, particularly with reference to the carbon content. The significant factor is the time spent above the start of active chromising which is about 760°C and this is illustrated in Fig. 4.

Obviously, the basic method of minimising the variations described, is to keep the size of the retort as small as possible, but this imposes the penalty of reducing the component/retort weight ratio, and hence, the viability of the whole process. In practical terms, an acceptable compromise must be reached, and this is achieved by having as wide a set of parameter tolerances as possible. When these are agreed, then the economics can be quantified and accepted or rejected.

2.4 The basic chemical reactions in chromising

It is not the scope of this research to re-examine the fundamental chemical reactions which have been proposed by various workers in this field(4,5,6,19,20). However, some consideration of them is necessary in order to appreciate the practical aspects of the process. As has been indicated earlier, the basic process involved in this work is an adaptation of the B. D. S.(5) and D. A. L.(4) processes. These initials are respectively derived from Becker, Daeves and Steinberg and Diffusion Alloys Ltd., by whom R.L. Samuel and N.A. Lockington were employed. Both processes consisted of a source of chromium, usually ferrochrome, and a refractory diluent such as alumina or kaolin and a halide either as its acid derivative e.g. hydrochloric acid or as its ammonium salt e.g. ammonium chloride or iodide. The refractory diluent takes very little part in the chemistry of the process, but as discussed in 2.5 it can have a significant effect upon the mechanics of the process and upon the final product.

On heating a chromium-enriched powder containing ammonium chloride, the first event is the sublimation of the solid halide at about 550°C. The gaseous compound then dissociates:

$$NH_4Cl \rightarrow NH_3 + HCl$$

Further increase in temperature leads to the dissociation of the ammonia and hydrochloric acid gases as follows: -

$$2NH_3 \rightarrow 3H_2 + N_2$$

and

$$2HCl \rightarrow H_2 + Cl_2$$

Combining these equations thus,

$$2NH_4Cl \rightarrow 4H_2 + N_2 + Cl_2$$

[solid] → [gas] [gas] [gas]

shows that from a relatively very small volume of solid there is derived a large volume of gas, all three constituents of which can be chemically active in their various ways apart from generating a pressure dependent upon their containment.

The chlorine, either elementally or as HCl will react with the chromium source to form gaseous chromous chloride as follows: -

$$Cr + 2HCl \rightarrow CrCl_2 + H_2$$

and from this reaction there is no volume change.

With the formation of chromous chloride (a vapour transport compound in C.V.D. parlance) the actual process of chromising can begin by virtue of two possible reactions: -

$$CrCl_2 + Fe \text{ (in component)} \rightarrow FeCl_2 + Cr \text{ (in component)}$$

This is termed the 'exchange' reaction.

The second is termed the 'reduction reaction'

$$CrCl_2 + H_2 \rightarrow 2HCl + Cr \text{ (in component)}$$

The desirability of H_2 is to provide conditions to minimise any substrate oxidation. H_2 does not reduce Cr_2O_3 at 1000°C and Cr deals with O_2 as Cr_2O_3.

The two gaseous halogen products of these last two reactions then continue to transfer chromium from the chromium-rich source to the ferrous-based component until the process is stopped by lowering the temperature or until a type of equilibrium is achieved. The simplest example of the latter is when the ratio of iron: chromium is the same on the ferrous-based component as on the source of chromium.

Attempts have been made both theoretically(19) and practically(20, 4) to determine which reactions are occurring at different temperatures, but, while it is possible to say the reactions which can not take place, in practice it is impossible to be precise because there are many other unquantifiable reactions which can and do occur(21). For example, unless the reaction container, usually termed a retort, is backfilled with dry hydrogen, there will be the presence of oxygen and nitrogen. The source of chromium can easily be contaminated with oxygen because of the mutual affinity of these two elements for each other etc.

Practically speaking, in the commercial application of the B.D.S. and D.A.L. processes and their variants, chromising does not commence until a minimum temperature of 750°C has been attained and then it is so slow as to be of little significance. The lowest known temperature used in a true production capacity was 800°C and that under very special conditions(21). The temperature range at which all chromising processes are carried out is 900-1100°C with the higher temperature being confined to the processing of super-alloys. For the carbon and low alloy steels 900-1020°C is the norm.

Attention can now be turned to some of the reactions at the interface of the compound or powder and the ferrous-based component. Here, it must be emphasised that virtually all that has been written on the mechanisms, is based upon examination of the end product and thus is speculative, but, in working to make a useful commercial product, other priorities can take precedence. Thus what follows contains experiences gleaned from industrial applications over many years(21, 22).

If the ferrous base is pure iron, then the situation is as described earlier and the 'exchange' and 'reduction' reactions take place and it is difficult to state the magnitude of either and its contribution to the end result. That result is a solid solution of chromium and iron with a composition gradient of the general form shown in Fig. 5.

If the ferrous base is a carbon steel, then complications arise and, because chromium is a strong carbide former, the reactions involving carbon exert a considerable influence on the resultant coating. If the carbon content is relatively low, say below 0.3%, then the coating may consist of two layers, the outer one a carbide of the general formula M_xC_y over-lying a chromium-enriched ferrite. The grain boundaries of this ferrite are usually thickened or delineated with carbide as is shown schematically in Fig. 6, As the carbon content of the steel increases to

0.4% and higher so the amount of ferrite decreases and the resultant coating is a carbide over-lying a zone of decarburisation as shown in Fig. 7.

The mechanism for these effects is that of absorption of chromium by the steel leading to the formation of the higher stability chromium-enriched carbide. The carbon source is the steel itself, hence the zone of decarburisation beneath the coating. However, reconsideration of the case of the low carbon steels shows that if a chromium-rich ferrite is produced there must have been active decarburisation at the steel surface and in turn this implies uphill diffusion by the carbon through the over-lying carbide. It also implies that the rate of decarburisation at the surface can become greater than the rate of supply (by diffusion) from the substrate. *Inter alia,* this rate of supply is influenced by the carbon content of the steel; the higher it is, the more likely a carbide coating will be obtained. Also the thickness of the steel section has a marked influence because of what may be termed the carbon 'bank' or reservoir. Thin sheet material of 0.15% C can produce substantially chromium ferrite coatings while heavier sections will have duplex coatings or a layer of M_xC_y carbide, both produced under identical conditions, indeed, within the same process retort and simultaneously.

There is a range or group of reactions which can take place when subjecting ferrous materials to heat treatment processes and simplistically they are as follows: -

a. $CO_2 + Fe \rightarrow FeO + CO$ [oxidising]
b. $H_2O + Fe \rightarrow FeO + H_2$ [oxidising]
c. $H_2 + CO_2 \rightarrow CO + H_2O$ [water gas reaction]

d. $CO_2 + Fe_3C \rightarrow 3Fe + 2CO$ [decarburising]

e. $H_2O + C \rightarrow CO + H_2$ [decarburising]

f. $CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O$ [decarburising]

g. $2H_2 + Fe_3C \rightarrow 3Fe + CH_4$ [decarburising]

h. $CH_4 + 3Fe \rightarrow Fe_3C + 2H_2$ [carburising]

i. $2CO + 3Fe \rightarrow Fe_3C + CO_2$ [carburising]

Clearly (h) and (i) are not of immediate significance in this context because the source of carbon going to form the carbide layer is the steel itself and not the gas generated by the powder surrounding it. A further consideration is that the chromium or ferrochrome used to make up the powder is of small grain size and hence of high surface area and thus quite reactive. As the temperature rises, so this metallic component will react with any oxygen (interstitial air) or water vapour which may be present broadly as in equations (a) and (b). Therefore, one is inclined towards reaction (g) at the steel component surface. Also, given that the ferrochrome powder can be, itself, low in carbon (0.1%) and, because of its high chromium content, it is a carbide 'former', it could react in accordance with reaction (h), the hydrogen gas within the retort acting as a transfer agent for carbon as the halide present acts as a transfer agent for the chromium and iron. It seems analogous to the carburising action in pack carburising where, in fact, oxygen acts as the transfer agent of the carbon from the charcoal to the steel or iron. Hence, the addition of barium carbonate to provide carbon dioxide on heating and to act as an 'accelerator' of the process.

An observation which may throw some light on the problem, relates to the pressures within the retort during the process cycle. In some work done in the early 1960s(21), an attempt was made to assess the pressure pattern during the cycle of the D.A.L. process. The idea was simple enough, namely, to weld a stainless steel tube to a small laboratory retort and connect it to a pressure gauge, thereby recording simultaneously temperature and pressure against time. One of the main reasons for doing the work, was to determine what might happen if there were power cuts, or at least, interruptions in the electricity supply.

Normally in industrial chromising, the charge is placed into a hot furnace and allowed to come to temperature with the furnace controller set at the desired processing temperature. This means that there is always a temperature gradient within the charge, and different chemical reactions taking place at the same instant of the process cycle.

In the pressure experiment, however, with a small laboratory retort weighing approximately 10kg, the heating was started from room temperature and raised at 100°C per hour. As shown in Fig. 8, the pressure rose to approximately 500mm water gauge (approx 0.05 atm) and levelled out at what was assumed to be the leak rate of the fusible seal. At about 700°C however, the pressure started to fall, went negative, followed by a fairly substantial explosion within the retort.

It was reasonable to presume that the explosion was caused by the ingestion of air and mixing with hydrogen in the retort to produce a gas of critical composition **at 700°C.** However, what was more difficult to determine was why there should develop a negative pressure of sufficient magnitude to ingest air. In answer to this question, it was suggested that a gas volume change occurred when the halide component (iodine in this case) started to react with the chromium with the production of chromic iodide as follows: -

$$2Cr + 3I_2 \rightarrow 2\ CrI_3$$

$$3\ \text{vol} \rightarrow 2\ \text{vol}$$

The chromic iodide would then decompose to the chromous state thus:

$$2CrI_3 \rightarrow 2\ CrI_2 + I_2$$

$$2\ \text{vol} \rightarrow 2\ \text{vol} + 1\ \text{vol}$$

The potential pressure changes can be seen quite clearly and if there is a gradation of temperature within a normal industrial charge then they will tend to cancel each other in their effect. The experiment did show however, the need to maintain heat input into the retort, once a temperature of about 500°C has been achieved. Charging a cold retort into a cold furnace should not be hazardous either, provided the energy input is maintained up to the process temperature.

Some further observations from practice, which help to indicate the conditions within the retort, relate to the expelling of combustible gases. Where a fusible glass seal is used, as in the D.A.L. type process, and when pressure within the retort has reached a sufficient value, gas bubbling out and through the glass is seen to ignite. Similarly, when using a sealed, controlled pressure retort, if there is a small crack in the retort casting, then gas which is forced out by the internal system pressure, will ignite to burn with a generally pale blue flame. The flame is not luminous suggesting that it is most likely from a hydrogen-rich source and not one containing significant quantities of hydrocarbons. Of course, carbon monoxide is a possibility, but thought to be unlikely in the presence of a strong carbide former as is chromium. Without doubt, the conditions are complex.

Turning now to the reactions of other constituents which may be present in steel being processed, reveals that some can have a significant effect, particularly the other carbide forming elements. Plain carbon steels of more than 0.3%C will show a greater degree of substrate decarburisation than alloy carbon steels of the same carbon content processed under the same conditions yet the carbide layer produced will be similar in thickness. The most likely explanation for this effect, is that the carbide forming elements, e.g. chromium, molybdenum, titanium, vanadium and tungsten to quote the common ones, act as a brake on the diffusion of carbon within the substrate because of the inherent stability of their carbides at high temperatures. However, once the carbon has reached the interface between the substrate and the inside of the coating layer, the 'kinetics' are solely under the influence of the chromium (and iron) component of the carbide coating.

This is well illustrated in principle with low carbon sheet steel in which the carbon has been stabilised with the traditional 4x its content with titanium. Here, solid solution coatings of 100µm are readily achieved with no grain boundary carbides thereby giving ductile coatings.

The elements phosphorus and sulphur are too low in the majority of steels to have any effect on chromising. However, in the free-cutting steels the sulphides can be found in the coating and thereby reduce the corrosion and oxidation resistance. The same comment applies to the leaded free-cutting steels.

Aluminium as a deoxidising agent has no effect upon the coating as such but in maintaining a finer grain size can help in the ductility of chromised sheet steel.

Manganese has little effect upon a chromised coating but it is interesting to note that the manganese content of a continuously regenerated and used chromising powder, gradually increases, showing that it is transported by the halide from the ferrous component. In this manner it can be said to behave similarly to iron.

Nickel in the amounts normally found in low-alloy steels has no significant effect on the chromised layer, but there is a suggestion that, because it tends to reduce the diffusion rate of carbon in the ferritic/austenitic matrix, it behaves in a manner analogous to the carbide formers described earlier.

Silicon, although a ferrite stabiliser, is too low in the low carbon steels to have any significant effect on the formation of the coating layer.

With regard to the gaseous elements present in the gases of the chromising process, the role of the halide has already been discussed and it is very unlikely that it has any direct effect upon the morphology or constitution of the ultimate coating. There are very often condensed phases of iron and chromium halides on the surface of the chromised component and if, for whatever reason, the surface of the component is porous, e.g. as a sintered compact, then halides will be found within the pores or interstices.

While these can cause considerable corrosion problems if not removed, they do not affect the coating as such.

Oxygen, which can be present as air if not removed by a vacuum exhaust or as water from dampness of the process powder or as reactive oxides e.g. iron oxide, can play a part in the chemistry of the process but has no significant effect on the coating morphology or properties.

Hydrogen, arising from water vapour and from the decomposition of the ammonium halide likewise plays a part in the chemistry of the process but there is no evidence that it affects the coating in any way.

Nitrogen, arising as it will, like oxygen, from air within the retort, or from the decomposition of the ammonium halide is an important element in regard to its effect on the morphology of the chromised coating(23, 24) and will be dealt with separately in a later Section 4.1.

2.5 The processing of small parts in chromising

The problems associated with the chromising of small parts were recognised in the immediate post-war years and mention has already been made of the so-called 'barrel chromising' in Section 2.2.

In deciding how to process a given small component, or even whether it can be processed satisfactorily, a number of factors have to be considered and the relative importance of these factors can vary from component to component.

The physical handling of the part will obviously reflect in the final cost and must bear a relationship to the intrinsic value of the part. For example, given that the chromising costs *per se* are the same, it is a much smaller percentage of the final component price if the base material being used is a super-alloy rather than a low alloy steel. The former can be viable while the latter is not.

The component geometry i.e. shape, is of considerable importance because of the effect of distortion occurring during the process. This is common to many heat treatment processes, but the times and temperatures used in metal diffusion processes are relatively longer and higher than in, say, hardening and tempering of steel parts. Because of this problem, the support of the chromising powder must be as firm as possible and the weight of other components and powder at higher levels in the process retorts kept within sensible limits. This again, because it can be a reduction in pay-load, increases costs per part.

When using a rectangular, square or round retort the normal practice is to place about 15mm of regenerated compound on the inside base followed by a layer of parts. These should be at a density such that the parts do not touch each other or the side of the retort. If parts touch each other, then there is an incipient danger of 'blind-spots' in the coating which at its worst manifestation, can lead to a type of welding. Schematically, this effect is shown in Fig. 9. Following the first layer of parts, a layer of compound is sprinkled on to completely cover them, and this is pressed down and levelled off, before adding the second layer of parts and so on, until the retort is filled to within about 50mm of the top. This headspace is filled with normal regenerated compound or with spent powder which is excess to requirements. Sometimes a steel-sheet cover is added as a loosely fitting lid to be followed by the standard cover for the retort. This again is shown schematically in Fig. 10.

Although care may be exercised in this packing operation, problems inevitably arise in what is a very subjective job for a factory operator, and where the throughput justifies the expenditure, specialist equipment has been designed and built to remove the problems associated with the human element. In the processing of chain pins and similar shaped components, magazine feeds are not difficult to develop, as are flexible tube feeds, all of which can be automated to a greater or lesser degree. Magnetic dispensers have also been used for placing small, flat plates in position within the retort. However, in spite of much ingenuity the labour cost looms large and in the retort method just described, errors by operators give rise to anxiety regarding the quality of the coating.

In the application of chromising to chain pins, firstly, because of large quantities, there is the opportunity to attack the process problems just outlined in a radical manner. Secondly, the shape of the part, with an acceptable mass and slenderness ratio (length/diameter), keeps distortion within acceptable limits. Thirdly, the concept of handling large numbers of such parts is already within the manufacturing experience.

It is at this point that an analogy can be drawn with electroplating, which saw its first application with the use of vats and hand-wiring for attachment to the cathode bars, followed by the subsequent development of barrel plating which requires very little hand work, and is therefore most suited to the coating of small parts in quantity.

Similarly with chromising; the first attempts with the use of a rotating retort could have been in Germany during the 1939-45 war, or not long after at the works of Diffusion Alloys Ltd in Eltham, South London. Although this work was not followed through at the time to a full-scale industrial application, it showed that the concept could be made to work, given the overall economic criteria being met. The parts to be processed, which had a higher slenderness ratio than chain pins, were pre-mixed with the chromising powder and placed in a refractory thimble some 250mm in diameter. A refractory lid or cover was luted in position with fire-clay cement, and the unit placed in a horizontal tube furnace which allowed rotation of the retort. The results were considered acceptable and the idea was taken up by a licensee of Diffusion Alloys in France, where many practical improvements were made.

Without doubt, these improvements were made possible by the concurrent development of methodology in the general and specific heat-treatment of both steel and non-ferrous metal parts. The robustness of rotary furnaces and the mechanical strength of the heat-resisting alloy retorts together with the adaptability to the specific process requirements of chromising, proved of considerable benefit to the processing of the small chain components.

2.6 The constituents of chromising powders and their behaviour over time

2.6.1 The source of chromium

In terms of commercial availability chromium can be obtained in virtually three forms: -

a. as commercially pure chromium which is produced by electrolytic means,
b. as a ferrochrome alloy of approximately 70% *Cr*, low in carbon, produced by a silico-thermic process, and
c. as a ferrochrome alloy of approximately 65% *Cr*, with carbon content of 4-10% produced by an electric furnace smelting process.

In terms of price, (a) is the most expensive and (c) the cheapest. Similarly, in terms of quality and reproducibility of given specifications, the order is (a), (b) and (c). Each of the three types can be obtained as powders or as granules by crushing, grinding and sieving with the finer grades being the more expensive.

The main contaminants of the two types of ferrochrome are slags from the reduction processes, and the cleanliness of a given supply source is very dependent upon the integrity of the manufacturer/supplier. There is much 'merchanting' of packages of ferro-alloys within the trade, and provenance of many of these is questionable. While this is of lower importance when the ferrochrome is for use in the steel industry, and the slags are fluxed away, in chromising, the slag particles can be in intimate contact with the parts being processed, and cause defects in the coating. Because of the metallurgical production process, it is virtually impossible to have a totally, slag-free product. Also, because aluminium and silicon can be in solid solution in the ferrochrome, where, in small quantities, they are innocuous, analysing for them gives no guide as to how much slag may be present. As a somewhat indirect route, it has been found that the general quality of the ferrochrome, particularly in steady state supply, can be assessed by the oxygen content, the slag being the primary source of this element.

An element which can be a deliberate addition to low carbon ferrochrome is silicon. This is added up to 1.5% where the ferrochrome is to be used in the ground, i.e. powder, form for the manufacture of welding rods to be used on stainless steel. It is said to make the lump ferrochrome more easily crushed to powder and may have some benefit as a fluxing agent in the welding process. In use, as a source of chromium for chromising, the difference in behaviour of the higher and lower silicon figure is negligible, and thus its use can come down to one of price and availability(21). Manufacturers of ferrochrome powders give the opinion that it is easier to crush or grind high carbon ferrochrome than the low carbon form, and the former is invariably lower in price per kilogram of chromium contained.

2.6.2. The refractory diluent

As already stated there are two main refractories used as a diluent in chromising. They are kaolinite and alumina, but they are not exclusive and others are possible, provided they have a sufficient degree of refractoriness (largely a question of their melting point), and do not react with the other constituents of the powder. In this category there have been used certain synthetic materials, largely alumino-silicates of the mullite group ($3Al_2O_3.2SiO_2$) which, although intended for use as refractory additives and as polishing or grinding media, can be obtained in a variety of crushed forms.

Kaolinite, obtained from naturally occurring deposits of kaolin, is a hydrated aluminium silicate, of the formula $Al_2O_3.2SiO_2.2H_2O$. There are certain constitutional variations, but they are not of significance in the present context. Kaolinite as sold commercially, is a fine white powder and, except within a narrow range, cannot be obtained in different mesh sizes. It also contains constitutional water and, during heating, this is driven off leaving the Kaolinite 'dead burnt', but also contributing some water vapour to the chromising atmosphere. It is also possible to obtain Kaolinite commercially in the pre-fired, i.e. water free, condition. This type has been used in chromising particularly in the processing of the super-alloys used in gas turbines, but there is no consensus of opinion as to its advantages, if any, in processing steel(21, 22).

2.6.3 The halides and their usages

The most common halide used in chromising processes is ammonium chloride of commercial purity, and added to the working powder in the crushed crystalline form. It is effective, of relatively low cost and also readily available.

Ammonium iodide has been used for many years in the D.A.L. process, but it is expensive and not readily available. The type used is 'chemically pure', largely because that is the only one available, and it is also added in the crushed, crystalline form.

Ammonium hydrogen difluoride has been used successfully for chromising but is not now in widespread use, if at all. There was some hesitancy on the part of the operators to using this agent, because of the rather poisonous and insidious nature of fluorides, although it is widely used in the aluminising of super-alloys without any apparent harmful effects. Again it is used in the crushed crystalline state and in the 'chemically pure' form.

Ammonium bromide has only been used experimentally, largely because of the poisonous effect of the bromides and bromine and also it is expensive when there are much cheaper agents available of equal efficiency. However, hydrobromic acid or bromine gas plus hydrogen, were used in attempts to chromise steel coil by the Lee-Wilson open coil annealing technique. This was in the late 1960s - early 1970s, but the project was abandoned after a relatively short time.

Dealing with halides in a comparative sense, it was claimed by Samuel and Lockington(5), that efficiency of the chromising process under standardised conditions but using each of the halides separately and in turn, was proportional to the atomic weight of the halide. Thus fluorine was the least 'active', through chlorine and bromine to iodine, as the most active. However, subsequent work to reproduce these results(21) failed to achieve any corroboration and on a larger, industrial scale no significant difference was observed in trials with chloride and iodide salts of ammonium.

Yet there are important practical differences in the use of the three common halides for use in a chromising powder, and they centre around their hygroscopic characteristics. The fluorides are relatively dry and not particularly hygroscopic so that powders remain drier between uses, and there is little adventitious decomposition. The iodides are also relatively dry, but if the processed parts are not cleaned of adhering salts, either by washing or immersing in a dewatering oil within 12-24 hours, then the hygroscopic nature of those salts comes into effect, and corrosion sites develop. In addition, in a damp atmosphere, the iodides react with carbides which can be present in the powder, to give iodoform (CHI_3). The chlorides are the most hygroscopic of the salts being discussed, and therefore chromised parts must be cleansed of the condensed chlorides on their surface as soon as possible, otherwise corrosion will set in. This is done in a hot, mild, alkali solution to neutralise any free acids resulting from hydrolysis, and is frequently followed by immersing in dilute nitric acid to neutralise any residual alkali. The precise methods of dealing with these problems of the halides, depend very much upon the parts being processed, and the throughput. If the latter is high, then special cleaning lines are justified.

2.6.4 Constituent behaviour with time

As has been stated earlier, the exchange reaction is probably the most important one in chromising, certainly when processing with powders and, although in much of the earlier literature the process seems to be treated on a solid-solid basis, it is, without doubt, a gaseous one. Therefore, in effecting changes at the surface of the component being processed, there are also analogous changes taking place at the surface of the chromium source. In effect, these changes are the reverse of the former with the concentration of chromium being reduced and that of iron increased. Examination of particles of low carbon ferrochrome after use in a working powder show this 'onion' effect quite clearly, but they can also show a substantial amount of 'tunnelling' as though there may be preferential sites at which the exchange reaction on the ferrochrome surface takes place. Another observation is that ferrochrome particles very frequently form agglomerates, despite the admixture of a refractory diluent, which also is occluded to give slag-like particles. Schematically these effects are shown in Fig. 11.

From these observations(21, 22), there follows the need for the steady state, regeneration of a working chromising powder, with the addition of fresh ferrochrome, refractory diluent and halide energiser, and this is something which can only be determined in practice by routine chemical analysis of the powders; certainly until a working balance has been achieved.

Regarding the possible 'slagging' action of the refractory noted above, some earlier work on aluminising is of significance(21). In this, the powder contained aluminium and chromium powder, ammonium hydrogen difluoride and small spherical balls of fused aluminia some 1.5-2.0mm diameter. In use, it was found that the aluminia balls became coated with aluminium, and therefore appeared metallic. Separation of the balls so coated, showed they could be used quite effectively as a source of aluminium. Since this could not have resulted from an exchange reaction, nor from a 'shot-peening' effect from tumbling, it must have resulted either by a reduction reaction, or a condensation effect.

A further observation(21), again with aluminising, which is of interest in this broader context, is that it is quite possible to aluminise steel/iron components using alumina powder and ammonium hydrogen difluoride. Here, the source of aluminium is the alumina and it must be being attacked and converted into a halide vapour by the fluoride.

From these observations, although it has not been positively demonstrated, it appears possible that the fine particles of refractory used in many chromising powders could also be 'metallised' during the process, and this would help to explain the agglomeration and sintering effects observed within the powder.

A powder which has been through a chromising cycle, has obviously lost some of its activity. The iron/chromium ratio will be higher and there will be less halide due to atmospheric loses, but it has been shown(21, 22) that this powder is still capable of chromising, and will only cease to function after five to six cycles. In the manner that these experiments were carried out however, it is very possible that the powder became oxidised. In this context, unless the retort is being evacuated of air and backfilled with nitrogen, a very important function of the halide is that, by its volatilisation, it drives out the air held in the interstitial spaces of the powder.

These interstitial spaces are important in the functioning of a powder. A coarse powder of average particle size 2mm will have a much larger interstitial volume than one of 0.5mm and it has been shown(21, 22) that, for an equivalent chromising activity a higher percentage (0.5-1.0%) of halide is required. For the finer powder to function in like manner and similar conditions, a percentage of 0.1% halide is sufficient. Since all of the solid halide will be volatised during the process at a temperature below that at which the metallic chromium is converted into a halide, there is much more gas expelled or exhausted with the coarse powders than the fine ones. In fact, it is only advantageous to use coarse powders if the retort or system is being evacuated, because finer powders can cause dust problems with the industrial vacuum pumps used.

2.6.5 The concept of 'throwing power' in chromising

The previous Sections 2.6.1 - 2.6.4, have introduced the porosity factor in chromising powders and since it has been established that chromising is undoubtedly a gaseous process, with virtually no solid-solid transfer, it is necessary to examine how the active gases function physically, or perhaps, practically.

The B.D.S. process(5), although packing the parts to be chromised together with ferrochrome and ceramic chips, utilised a flow of hydrogen, both to carry the hydrochloric acid gas and, to move the active gas, chromous chloride, through the mass. In effect, this was efficient but wasteful.

The D.A.L. process(4), although open to criticism on the grounds of oxidation of the steel surfaces to be treated, was efficient but less wasteful of raw materials. It was, however, a dusty process, employing as it did, a substantial percentage of fine kaolin as the refractory. In this process was embodied the idea that, by using finer powders and thereby reducing the interstitial space, the active gas, generated very closely to the component surface, would have a shorter distance to travel. Also, it was argued that, when processing turned or formed parts, the powder, being fine, would pack into crevices and re-entrant corners and thereby generate the active gas, and hence obtain a satisfactory, all-over coating of even thickness. This is analogous to the concept of 'throwing power' found in electroplating theory and practice.

There have been two what might be termed 'purely gaseous' methods of chromising put forward. One, already described earlier, was for the chromising of steel coil and used hydrogen and bromine with fan induced circulation forcing the active gas through the open-wound coil. The other was developed by Galmiche(25) in France at L'Organisation National pour L'Etudes et Recherches Aéronautiques (hence its name, the O.N.E.R.A. process), in which hydrogen fluoride gas was the active exchange medium. This was thermally circulated over a source of chromium, with the parts to be coated suspended above. Neither of these processes achieved commercial success and, as already suggested, they both suffered from the same problem as in electroplating, namely 'ghost' marks of low coating thickness where the working surface was in contact with a separator or support.

In an attempt to determine what might be termed the 'throwing power' of the D.A.L. powder(21, 22), thin strips of low carbon steel were pushed vertically into a bed of regenerated powder, such that 50mm or so was in the free space above the powder contained in the retort. This is shown in Fig. 12. The retort was exhausted of air and back-filled with dry 95% nitrogen/5% hydrogen, immediately placed in a furnace at 1000°C and allowed to heat naturally and held at temperature for 8 hours. After cooling, stripping out and cleaning, the steel strips showed measurable (i.e. detectable) chromising for only 12-15mm above the powder line. This seems to indicate that unless there is a forced circulation within the system, relying upon a thermally induced circulation is not very productive. Put another way, it is obvious that the carrier gas (molecules) must have to make a great number of journeys between chromium source and work piece to achieve that which is achieved in practice. Therefore the fine powder approach appears to be the correct one in static processes, making sure that the powder is in contact with the critical surfaces of the work piece.

Fortunately, in the context of the project described herein, because the chain pins are of low slenderness ratio, it is possible to consider moving **them** in relation to the active powder, thereby achieving the ideal situation for a coating free of deficiencies of thickness.

3 EXAMINATION OF CHAIN PINS FROM SERVICE

3.1 Presentation and Metallurgical Examination

In the Introduction there was given how this project started with a few chain pins having been extracted from a timing chain which, it was claimed, had given a very good service life. These had been examined metallurgically and also compositionally by electron-probe techniques. All that was made available however, were some photo-micrographs and the electron-probe analysis. There were differences in the microstructures and analysis purporting to come either from the same chain or from different chains made by the same manufacturer. It was suggested that the supplier was not European, which implied that it was Japanese because of what was known commercially of the buying policy of the car manufacturer.

The data made available is given in Table 1 and the structure of the coating(s) are shown diagrammatically in Fig. 13. The structure shows a quite distinct outer layer of approximately 1-2μm overlying an inner layer of 12μm. This structure is revealed by etching in Murakami's Reagent (potassium ferricyanide 10gm, potassium hydroxide 10gm and water 100ml). The inner layer itself also consists of two zones, the division being a broad band of more or less columnar form. The delineation of this is much less distinct than that of the outer layer but is nonetheless quite visible and reproducible on repolishing and etching. It is not an artefact.

The compositional data given shows a very high chromium/iron ratio in the outer layer with the presence of nitrogen. The percentage of carbon was not given and it was not known if and how the obtained values had been normalised. No hardness values were made available.

Based on previous work(21), it was clear that the coating had been produced using a low carbon source of chromium and the very high chromium/iron ratio in the outer layer strongly indicated that the metallic constituent of the processing powder was pure chromium. This fitted very well with the origin of the pins/chain as being Japan as it was known that chromium powder was in use there.

It also indicated that there was a variation in the metallography of the coating among the two to three hundred pins in a given chain. The coating thickness could vary some plus or minus five microns about a mean value.

The development target set out was to produce a chain pin as had been shown and described in the belief that that would furnish a timing chain with superior properties. It was also somewhat implicit that there should be no marked increase in costs.

3.2 The wear and failure pattern of timing chains

Timing chains can have several modes of failure. There can be what may be termed 'steady state' wear and a catastrophic wear. The latter is almost entirely due to lack of or carelessness in the maintenance and is outside the scope of this work. Also there can be a further serious failure by a purely mechanical means such as the fracture of a side plate or bush. Again, this is outside the scope of this work.

A steady state of wear in a chain manifests itself by an increase in length. Up to a point, this can be taken care of by the introduction of a tensioner which may be hydraulic or spring activated. However, this does not prevent wear and a final criterion is the relationship between the chain roller and the sprocket teeth with which it engages. This is the pitch distance of the chain and can be defined as the distance between the pin centres when the chain is in moderate tension.

The four basic components of the chain are shown in Fig. 14(a) and in the assembled condition in Fig. 14(b). The distance 'p' is the pitch referred to above. The inner plates are termed connecting links/plates and the outer ones are the riveting links/plates. In assembly, the pins are so struck end-on, that the end swells and is thereby fixed into the riveting plate. There is no relative movement between the pin and riveting plate in service. It can be seen that the roller is free to rotate around the bush but the bush is not free to rotate at will around the pin, because it is compressed between the riveting links. This causes a restricted arc of rotation of the bush round the pin, dependent upon the configuration of the sprockets around which the chain passes. Some typical examples are shown in Fig. 15 and the possible arcs of movement are shown in Fig. 16.

Thus it can be seen that, with a chain in operation and therefore in cyclic tension, there is a restricted area of contact between the bush and the pin. In fact, in theory and in a highly idealised situation, there should be but a very narrow band of contact between the two parts, which sweeps out at the relevant arc of the two contacting surfaces. In practice, however, this does not happen, partly because of the tolerance limits of the component parts, and also because of the slight sideways location of the chain on the sprocket. This gives rise to variations in the stress within the side plates of a given link of the chain, i.e. the tension is not always precisely linear, and so a rocking motion, albeit very small, can develop. The typical wear patterns on a link pin are shown in Fig. 17 and will be seen to correspond with the points made above.

Some aspects of manufacturing can have a marked influence on the wear pattern. Pins, having been cropped from straightened wire, are centreless ground and although it is possible to have a degree of out-of-roundness, this is consistent along the length and not so much of a problem. With this component, surface finish is the most important factor and this will be discussed further. The bushes are made from rolled strip which is again cropped to length, and roll-formed about a mandrel. There is considerable pressure applied during this forming process to achieve the required degree of roundness, but nonetheless, the inside face is in compression and, not moving so much in relation to the hardened mandrel, it is not planished as much as the outer face. Hence, with the amount of grain rolling on the inside face, the grain size of the raw material is critical in achieving as good a surface finish as possible. It is this inside face which takes the full transmission load of the chain. The roller which is around the bush and, which by definition, is free to rotate, has a nominally wider contact area with the bush and is only under stress when in contact with a sprocket tooth.

By the wear which can take place between the pin and bush there will develop a lengthening of the chain i.e. the dimension 'p' in Fig. 14(b) will increase. This will lead to a lack of proper register of the links as they ride over the sprockets, both driving and driven. This, in turn, imposes more wear on the rollers and the sprocket teeth. Thus it can be seen that the main criterion in the working life of the chain is the amount of wear which takes place at the pin/bush contact zone and that a simple way of assessing this is by measuring the effective extension or lengthening of the whole chain, either after a period of service, or after running on a test-rig.

In principle, test-rigs are simple, consisting of a driving and an idling sprocket, around which the chain is looped. The idling sprocket can be loaded via a yoke and thereby apply a tension to the chain. From this test procedure, time/extension curves can be obtained, which have many similarities with creep curves. Typical examples are given in Fig. 18.

The first part of the curve can best be described as 'bedding-in', and it is during this phase that any slight roughness or possible mis-alignment will be subject to the full load on the chain, and therefore suffer a much higher rate of attrition. The height of the transition from curve to straight line is, indeed, a good measure of overall quality of manufacture, both with regard to tolerances and surface finishing procedures. Another practice which helps to reduce the height of this step, is to pre-stretch the chain as a final stage of manufacture, and this also must result in the chain length lying within a tolerance band. The straight part of the graph is a steady state wear rate, being proportional to the severity of the operating or test conditions and the resistance to wear of the pins and bushes, particularly the former. The flatter this line is, the better the wear resistance of these critical components. The final part (not shown) is an increasing rate of wear and takes place when the hard coating of 'chromium carbide' has been penetrated, and there is direct contact between the bush and the core material of the pin.

In service, the chain is subjected to more of a pulsating load than the test described above, this being caused by the power stroke of the cylinder/pistons as they fire in sequence. Experience dictates that diesel engines have a stronger pulse effect than petrol engines, and hence they are, in practice, a more stringent test-bed for any innovative chain developments. The work cycle of a taxi is particularly effective in this context.

It is, of course, possible to impose a pulsating regime on an engine test-bed or, with increasing sophistication, on a laboratory test, but in the final analysis, as with many other engine components, the manufacturers insist upon appropriate road trials anyway, and therefore this may as well be part of any development programme.

4. THE DEVELOPMENT OF THE NEW PROCESS

4.1 Consideration of previous literature

Within the considerable volume of literature, which Castle and Gabe have shown to be available on the subject of chromising(1), there are two papers which have a significant bearing upon the present work(23, 24) and which will be discussed in some detail. The first by Komen *et al* records work carried out at the request of an Israeli licensee of Diffusion Alloys Ltd and Dr B.Z. Weiss spent several days at Diffusion Alloys studying various aspects of chromising before setting up the research project. The second by Tacikowski and Liliental(24) which was carried out in Warsaw, probably was a sequel to the marked increase of interest in the application of chromising to improve the life of metal forming tools in the 1960s. This was particularly so in the Communist Bloc and it is interesting to note that of the eight references given in this paper presented in 1976, four are Russian, one is the work by Komen and Weiss(23), two are virtually archaic and none are after 1968.

Tacikowski's work is of wide scope and well structured but very little information is given on how the chromising was carried out, except that ammonium chloride of unknown quantity was used, together with three variants of refractory filler, namely, kaolin, silica and alumina. Komen's work is narrow in scope, but detailed in reporting and analysis together with an in-depth account of the chromising operation. Here ammonium iodide was used as the halogen source and kaolin as the refractory diluent or filler.

Taking the narrow range of experimental conditions used by Komen and abstracting as near as possible the same or similar area in Tacikowski's work, they both arrive at results which are structurally close to each other. They are also in broad agreement with earlier work carried out in the school of Dubinin in Russia(26).

Broadly, although the metallography as presented was not particularly good in any of the papers, it was shown that, under certain conditions, the chromised layer or coating could be of either one, two or three 'phases'. If the carbon content of the steel was low (below 0.1%) and the decarburising power of the chromising powder and treatment conditions were high, then a carbide free solid solution of chromium and iron would be obtained. If the carbon content of the steel was medium to high (0.25 - 0.8%) and the decarburising power etc. was low then a carbidic layer would result which may consist of one or two phases, namely M_7C_3 and $M_{23}C_6$ with the latter always overlying the former. That is, the $M_{23}C_6$ was the outer phase. Finally, if the carbon content of the steel was medium to high and the carbon content of the ferrochrome or chromium in the chromising powder was low (below 0.8%), then it was quite possible for a third phase, M_2N, to overly the $M_{23}C_6$ carbide, making a nominal three phase or three-fold layer.

Working on the basis of X-ray diffraction there is no disagreement regarding the identification of the M_7C_3 and $M_{23}C_6$ carbides where M is (*Cr.Fe*), but on the constitution of the nitride M_2N, there are differences of opinion. Tacikowski throughout the whole paper used the symbols 'M_2N' and *the term* 'M_2N nitride', without attempting to define '*M*', whereas he goes to some length to define and quantify '*M*' in the two carbides. Komen, however, is much more specific, referring to the outer layer quite definitely as beta-Cr_2N which has a close-packed hexagonal lattice. He also goes on to dispute the claim by Kanyakina and Dubinin(26) that the phase contains carbon and is therefore a carbo-nitride to be written as $Cr_2(N.C.)$. However in a table of analytical results the composition of the metallic component of the phase i.e. the 'M' of M_2N is given as follows: -

	%	%
Cr	71.4	81.2
Fe	16.0	7.1
	87.4	88.3

Thus he shows that his 'Cr' in Cr_2N is strictly 'M' i.e. $(Cr.Fe)$ which is what one should expect in a diffusion system of the type under consideration but he will not allow that the 'N' of Cr_2N may be $(N.C.)$.

As further confirmation that nitrides can be present in chromised coatings, some work carried out at Diffusion Alloys about thirty years ago(21) when a low carbon austenitic stainless steel (18/8) was chromised using a low carbon ferrochrome, the resulting coating of approximately 25µm was shown to be beta-Cr_2N. It was hard and smooth with a somewhat slippery feel to it and it showed useful anti-galling properties. It went on to be used for fasteners for containers holding radioactive waste.

From this brief review of past work it appears quite possible that coatings of carbide, carbide and nitride and nitride can be achieved from chromising provided the correct conditions are generated within the process retort and with the selection of the most appropriate substrate.

Furthermore, it is an obvious inference that almost from the start of industrial chromising, when low carbon ferrochrome and/or chromium powder were used to make up the compound and the process was being applied to medium-eutectoid carbon steels, carbide coatings with supposed outer layers of nitrides or carbo-nitrides were being obtained. It was a case that they were not recognised as such because the most commonly used etchant for determining coating thickness was, and still is, 3-5% Nital and this does not reveal the structural characteristics of the carbide layer.

4.2 Consideration of possible options

Because there was an already operating chromising facility and also that no major design or material changes could be allowed with regard to the components being processed and assembled into existing roller chain manufacture, any new process had to broadly fit in with the existing *modus operandi*.

The steel from which pins were/are made is C60E according to EN10083 Pt 1, the composition of which is: -

Carbon	0.57 - 0.65%
Silicon	0.15 - 0.40%
Manganese	0.60 - 0.90%
Phosphorus & Sulphur	0.035% max

This is purchased as oversize and given a sizing re-draw before being cropped to length and centreless ground to a diameter which accommodates the increase in size resulting from chromising. After chromising the parts are hardened and tempered to a core hardness of 550-700 HV. They are then barrel finished, which operation is discussed later. The pins for use in chains for other types of service, may be carbo-nitrided and thus it can be appreciated that the various mechanical properties used in design calculations must be maintained whatever changes are made in intermediate processes. At this stage of the project, no serious problems were anticipated with regard to these aspects. The carbon content in relation to the pin size was sufficient, and the modest alloy additions were adjudged to be quite acceptable.

The existing chromising facility which had been operating for several years consisted of a bank of rotary furnaces into which sealed retorts containing pins and powder were placed for an appropriate time/temperature cycle. The ferrochrome used was of the high-carbon type and the refractory diluent was a proportional mixture of fine alumina and a proprietary crushed barrel-polishing media, probably a synthesised alumino-silicate. The source of the halide was ammonium chloride. Unfortunately, there were no in-house reports or other documents detailing how or why the process parameters had been chosen and control was exercised on the basis of a process specification and raw material purchase specifications.

Prior to placing the cold retorts into the hot furnaces, they were exhausted of air and back-filled with 'formieren' gas, which is nitrogen with a small percentage of hydrogen. Because the retorts, made of a heat resisting nickel/chromium alloy, were closed off as shown in Fig. 19, there was a safety valve and exhaust outlet fitted in the bolted-on cover plate. Mounted centrally on the inside of the cover plate was a baffle system which sought to keep the mass of powder and pins within the hot zone of the furnace as it was rotated. When the furnace cycle had been completed, the retort was put to cool down in a fan-assisted chamber, then opened and the contents discharged onto a vibrating sieve or screen to separate pins from powder. The pins were sent to heat-treatment and the powder for regeneration. The powder was subject to a fairly strict control with regard to its batch identity, each batch being a volume/weight suitable for one retort change. After a prescribed number of cycles a given batch of powder was scrapped.

Fundamentally, there was nothing wrong with the basic process, particularly its methodology and mechanisation, and it had probably been copied from the French company, S.E.D.I.S. together with help from the furnace supplier Aechelin. However, because there was so little operational data available, most of it in the operators' memory, it was decided that a review should be made to record as much as possible, with particular reference to defects and their causes, before any process changes were introduced. This has formed the basis of a separate report(27) but some of the important findings and observations are made below because they have a bearing upon decisions made in the development of the process to produce a three-fold layer chromised coating.

The existing coating produced, using a high carbon ferrochrome, was a nominal 12-15μm and, as expected, consisted of one layer when etched in Murakami's reagent and was very probably M_7C_3 type.

There was, within a given batch of processed pins a wider variation of coating thickness than would have been expected in a system in which the retort was being slowly but continuously rotated. This led to a redesign of the heat shield fitted into the retort to reduce heat loss within the charge. It also led to a practical examination of the movement within the charge resulting from rotation. This was carried out using a glass container of the same internal diameter as the retort. As expected, there was a cascade movement or slide of pins and powder down the face of the charge but no significant longitudinal movement. Also it was obvious that there was a rotational centre of the charge different from that of the retort and this is shown in Fig. 20. This core area was slow moving but given the process time of several hours it dispersed and moved into a more active zone.

While the movement of the pins relative to the powder is in itself a good feature because it stops pins covering each other, which can lead to 'blind spots' where the coating is thinner, it did cause a problem, namely surface damage. This arises when pins cascade down the charge face and impact against each other. The temperature is high, 1000°C, and the steel is therefore soft and characteristic elliptical depressions are formed where the end of one pin impacts against the cylindrical face of another. This same effect also happens in various transfer functions during the production process, but precautions can be taken to minimise it. Therefore, this problem led to a rethink when formulating the new process.

Another serious problem on quality control, was caused by slag contamination of the high carbon ferrochrome. This has been referred to earlier in Section 2.6.1 and arises from the smelting practice in producing this type of ferrochrome. The normal end use of high carbon grades is in iron (cast) and steel making such that, as a furnace or ladle addition, any slag contamination passes into the process slag and is removed. However, in crushing and grinding for use in chromising, the slag is reduced to the mesh size and it is very difficult to remove in spite of the substantial difference in gravity between it and the ferrochrome. Frequently, because it is within the solid lumps of the ferrochrome, it remains attached to the metal through the comminution process.

Although the melting point of the slag is higher than the chromising temperatures of about 1000°C, nevertheless, it softens and flows over the pin surfaces. This process may well be assisted by the reducing conditions within the process retort and the presence of halides could exert a fluxing effect on the slag. The net effect is areas of glassy contamination, with the steel surface of the pin fluxed away to depths of up to 100µm. Sometimes the slag produces concretions of powder particles adhering to the surface which, although they may be removed by subsequent barrel finishing, leave a depressed area and a poor quality coating. These defects are shown in Fig. 21 taken from the report mentioned earlier.

Another problem which could arise was due to actual and incipient corrosion of the pin after grinding and before chromising. Parts which have been fine ground or barrel finished, and are thoroughly de-greased, are prone to condensation corrosion. This can occur if the ambient factory temperature drops overnight, or over the weekend, and particularly during the winter period. Also process exhaust gases e.g. from furnaces ducting into the workshop space and steam from wet processing can all exacerbate this problem. Probably the best way of dealing with it is strict rotational working practice and good stock control to keep work in progress at a minimum. If this is difficult to achieve, then some form of atmosphere-controlled store can help. The defects within the coating caused by this pre-chromising corrosion are illustrated in Fig. 22. In a similar manner, after chromising, parts should be cleaned as soon as possible because of the hygroscopic nature of the condensed halides found on the surface. In this context, chlorides are generally more of a problem than iodides and fluorides. Probably one of the easiest ways of dealing with this aspect of the process cycle is to get the parts through heat-treatment as soon as possible. This volatilises the halides and the oil quench confers a barrier effect to adventitious moisture. These types of problem were dealt with by a combination of the practices outlined above.

Other problems, strictly, not caused by the chromising process, but included here for completeness, were primarily mechanical and occurred in the pre- and post- chromising operations. Typical examples are rough grinding, incomplete grinding, spiral grooving from the lateral feed wheel, elliptical impact damage etc. In the post-chromising operations, it is possible to develop a 'glazed' oxide during heat treatment in spite of a controlled atmosphere and in that it is random it is probably caused by the part remaining in the furnace longer than it should i.e. a mechanical reason.

Also in post-chromising, damage to the coating can occur during barrel finishing, particularly when using the 'super finish' or 'High G' centrifugal method. Too high an impacting of part on part (or media on part, but much less common) leads to exfoliation particularly of the outer or 'nitride' layer when present. These very shallow depressions are white to light-grey in colour and are very distinctive. Quite common is removal of some of the coating around the shoulder at the end of the pin, but this is not a critical area, and can be ignored. However, it shows how near to the critical, mechanical properties of the coating finishing operations are pushed, much of it to reduce process times and hence work in progress.

In deciding upon the preferred option it was obvious with an already existing plant and practice capable of producing chromised chain pins that, in spite of any shortcomings, the route should be to use that plant or at least try to in the first instance. As already discussed in Section 2.5 the rotary type furnace has some distinct advantages over the box system using side or front loading bell or muffle type furnaces when processing small parts such as chain pins. With the latter, there is the uneven temperature distribution from corner to centre and although this can be ameliorated somewhat by using round retorts and even the doughnut type, the lack of relative movement of the charge confines a part to where it is put. The Japanese, persisting with sealed rectangular boxes/retorts, have developed sophisticated mechanical box filling equipment to scatter the pins on successive layers of compound, but touching still occurs and the temperature distribution problem produces a wider than ideal range of coating thickness, as noted in Section 3.1.

The charging of the retort with the rotary system is much quicker and simpler than with the box system since powder and pins can be fed in simultaneously with the retort in the upright position. Then with the head baffle in position and the retort closed, it can be turned to the horizontal position and rotated cold to ensure a fully mixed charge of powder and pins.

The powder mixing facilities, while not ideal, were considered adequate at this stage of the project, particularly when, with the rotary process, the powder is in a continuous state of being mixed during chromising.

With the existing process, and indeed in other chromising facilities, it is the common practice when preparing a new batch of powder, to 'pre-fire' it at the temperature at which it is likely to be used. The time at temperature is not critical provided the mass attains the temperature throughout. The powder, when cold, is put through a suitable sieve to break up any lumps and it is then regenerated with fresh ferrochrome, refractory diluent and halide, either according to the results of chemical analysis, or based upon established practice. The reason for this procedure is because when a full mass of new powder which has not been pre-fired is used, although the overall chromising characteristics are likely to be satisfactory, the level of sintering of ferrochrome particles onto the surface of the steel part can be unacceptable. This is particularly the case in processing low carbon steels where the chemical composition of the coating at its outer face approaches that of the ferrochrome from which it is derived. Its crystallographic structure is also similar. When processing carbon steels, the problem of sintering of the surface is much less acute because of the formation of the carbidic layer. Its composition has a chromium level much higher than the ferrochrome used and its crystal structure is quite different except when using high carbon ferrochrome but even there, sintering onto the surface is not normally a problem. Another reason for pre-firing a new batch of powder is to develop the condensed phases of the chromium and iron halides which play a significant role in the early part of the process cycle of chromising. They are the initial source of chromium.

With continued use of a compound, there is continued regeneration to maintain the critical constituents at their required level. In theory, and in practice at some facilities, the compound is used repeatedly, thereby simply developing a stock, surplus to requirements. This is taken out of circulation and put to scrap. However, what may happen is that the powder develops too high a proportion of fines and becomes too dusty for ease of use. When this occurs, depends entirely upon the constitution of the powder, with particular reference to the refractory and how it breaks up with use. It is an operational decision when to dispose of it and start afresh, and some operators will scrap half of their working stock bank, and replenish it with new.

4.3 Initial trials and results

In order that current production could be maintained and no rotary furnaces taken out of service and in spite of what has been written earlier on the shortcomings of the rectangular box or retort system, it was decided that initial trials should be conducted using such boxes in conventional static muffle-type furnaces. There was sufficient background history and experience to be confident that this course of action would not in any way produce invalid results nor be incapable of being translated in principle at least across to the rotary or dynamic process. Therefore, a powder was prepared according to the following formula:

70/30 Low carbon ferrochrome, 60 mesh	50%
Alumina - calcined	49%
Powdered Ammonium Chloride C.P.	1%

This was pre-mixed in a rotating drum and pre-fired at 1000°C for 10 hours total time, being charged into a hot furnace at 1000°C. After cooling, it was passed through a vibrating screen of 20 mesh to break up any lumps and regenerated at a level of 10%, i.e. 5 kilos ferrochrome, 5 kilos alumina but 1 kilo ammonium chloride per 100 kilos of compound. This formulation gives a metallic composition of:

34 - 40%	Chromium
15 - 18%	Iron

It is worth stressing at this point that because the alumina, or for that matter any refractory diluent is effectively inert in this process, the 'active' ratio of *Cr:Fe* is always of the order 7:3. In use, particularly if the exchange reaction discussed in Section 2.4 is prominent, the iron content of the powder can rise above 20% and the *Cr:Fe* ratio thereby weakens to 2:1. Practical experience however has shown this to be a workable powder in a wide range of industrial/commercial applications. After pre-firing a powder, there is also present a small but significant amount of water soluble metallic halides, the practical effect of which has been mentioned in Section 4.2.

The box/retort used was the cover and tray system as illustrated in Fig. 2 and the dimensions of the inner box were 450mm x 250m x 250mm. Packing was done by hand with an initial 25mm of compound levelled on the bottom followed by a layer of pins, followed by a 12mm layer of compound, then layer of pins and so on to within 60mm of the top. A final layer of 30-40mm of compound was put on to reduce the problem of air ingress and the box closed off with a thin steel sheet. A small quantity of old, unregenerated compound was put on the steel sheet, again to reduce the ingress of air (particularly oxygen). The weight ratio of pins to powder was approximately 1:1 but, of course, the volume ratio was of the order 1:4.

The weight ratio of parts to powder of 1:1 is one which has been a characteristic of industrial chromising for many years. It is far from being sacrosanct but has been found to be a useful rule-of-thumb in starting the processing of new parts until experience indicates a movement either way may be advantageous.

Having packed the inner box as described, closed it and sealed it as per the D.A.L. process described in Section 2.2, it was placed in a hot muffle furnace set at 980°C and allowed to heat naturally. The furnace regains its set temperature after about 100 minutes and the retort is allowed to soak until the expiry of twelve hours from charging, then removed and allowed to cool naturally. When fully cooled, the box was opened, cleaned of burnt compound, the contents emptied onto a vibrating screen and the pins separated from the powder.

Examination of these pins showed them to be reasonably smooth with a degree of sintered-on ferrochrome which experience indicated would be readily removed by subsequent barrel finishing. The 'colour' was a uniform silver-grey and there was no evidence of exfoliation of the coating. Several pins were sectioned for metallographic examination. Unetched, there was evidence of a hard coating because of a slight amount of polish relief. There was also evidence of very small inclusions, particularly near the outer surface. After etching in Murakami's reagent the structure revealed was as shown diagrammatically in Fig 23, with a total coating thickness of 15µm and an outer layer of 3µm.

A quantity of the pins were put through the hardening and tempering cycle followed by barrel finishing to R_z(max) 1.0µm. Some of these were likewise sectioned, polished and etched and again the coating was of the same dimensions but now overlying a tempered martensitic structure as expected. The core hardness was 640 D.P.N. which was within specification.

It could be said that, structurally, the three-layer coating required by the car-engine manufacturer and described in Section 3.1 had been achieved since no crystallographic requirements, or for that matter, compositional ones had been specified. This position was not considered a satisfactory outcome, however because of the industrial/commercial potential involved.

Accordingly, the project sub-divided into more specific stages as follows: -

A. Evaluation of repeatability and translation of process to the rotary furnace technique.
B. Evaluation of the coatings' performance in laboratory and engine trials.
C. More detailed examination of the coating.

Of these, the commercial pressures were to concentrate on A and B.

The fulfilment of A was achieved by the work being carried out at a different facility such that it did not interfere with normal production. Also, the level of confidence established was such that the quantities of pins produced, could be used in chains of a somewhat lower specification than those needed in original equipment (O.E.). During this phase of the project, the compositional changes in the compound were monitored together with the resultant coating, and these are shown in Table 2, having been extracted from the routine chemical analysis carried out daily as required. The range of coating thickness is also given for the period and it was found that in spite of a slowly increasing chromium content of the powder and also a slight increase in the *Cr:Fe* ratio, there was no corresponding increase in the average coating thickness over that same period. This illustrates clearly the wide tolerance of the chemical composition of the chromising powder with regard to the metallic content and in this case the regeneration rate was reduced from ten percent to eight percent. The result was that the metallic chromium content of the powder eased back slowly to the original 35-40% range, again with no change in the coating thickness or its desired morphology.

One of the conclusions, or rather observations, which can be made regarding the behaviour illustrated above, is that the functioning of the process to produce a required coating thickness, is more dependent upon temperature and time than quite noticeable variations of chemical composition of the powder. These comments relate to a given method of processing, and at this stage, it was decided that sufficient experience had been gained in relation to the performance of the process parameters and the achievement of the required coating morphology that it could be translated from a static box retort to the rotating cylindrical retort.

The only problem, which arose in the static process, was the development of what can only be described as a 'fish-scale' defect. This is shown schematically in Fig. 24 and is reminiscent of the 'fish-scale' defect caused by nucleation of hydrogen sometimes found in vitreous enamel. To the naked eye, the defect consisted of very small elliptical bright spots where the coating had exfoliated after removal from the retort. It is generally accepted that carbide coatings on chromised components are in compression and the saucer-shaped fracture lines would seem to confirm this. However, there can also be found in carbide coatings cracks which are radial or normal to the surface and which are wider at the surface. This is usually taken to indicate that a coating is in tension and therefore some caution is needed in offering an explanation for the defect solely on the basis of inherent stresses. Careful examination of all available process control data failed to reveal any aspect which could correlate with the few occasions when the defect occurred. Fortunately, as the work progressed it proved to be a characteristic of the static box retort and no further investigation was made.

Concurrent with the process development work just described, tests were carried out on test rigs in the laboratory to see how the assembled chains, using the 'three-fold·layer' on the pins, would behave. The results of these tests (as have been described in Section 3.2) were very encouraging with the achievement of much lower wear rates than the then standard chain.

At this stage, there was cautious optimism that Stages A and B set out earlier had been partly completed and that the rotating retort should be evaluated. Accordingly, a new quantity of compound was prepared, pre-fired and regenerated. Also at this stage it was considered prudent to work with one retort only. In all other respects the process conditions were as for the box process except that charging the retort was done with a specially designed hopper in which parts and powder are fed simultaneously. This method is very much quicker than the laborious process used in packing a rectangular box retort.

In the established process, using high carbon ferrochrome, after securing the cap on the retort, the air inside is exhausted by a vacuum pump and 'formieren' gas is admitted, and although this had not been done on the box retort, it was thought prudent to follow established practice. Furthermore, it was part of this practice to operate at a pressure, within the retort during the chromising cycle, of ~3 atmospheres. It was not known within the company why this was so and, as an installation, it was probably the only unit in continuous production which did operate at a significant hyperbaric pressure.

The retort was charged into a furnace operating at 980°C and allowed to heat naturally. During this period, the pressure increased to ~5 atmospheres in about 60 minutes when the relief valve came into operation allowing a bleed off to atmosphere. The time for the furnace to regain temperature was 55 minutes and the whole cycle time of 10 hours run to completion. During this period, the retort was rotated as earlier described, the time for one complete rotation being about 15 minutes. On completion of the cycle, the retort, still under pressure, was removed and placed in a forced draught cooling shed. An interesting observation made when the hot retort was removed from the furnace and under pressure, was the issue of an obviously combustible gas from a small crack in the nose of the retort. The flame was lambent, of pale colour, slightly bluish and non-luminous. Of gases (combustible) which could be present, it was thought to be hydrogen. It was very similar to the effect obtained in an experiment conducted many years ago(21) where a rectangular retort with a fine powder inert seal was pressurised with hydrogen at 12mm water gauge during its process cycle. The escaping hydrogen burned on the surface of the seal with the same type of flame.

When cold, the retort was opened and the contents discharged onto a vibrating screen for separation. This was easily achieved, as there was very little aggregation of the pins and compound. The latter was friable. The pins were of a semi-bright silvery appearance with no blue from oxidation and there was no sintering of ferrochrome onto the surface although the surface was slightly rougher than the original surface of the pins. On metallographic examination, the coating was 13-15µm and of the desired three-fold structure, with an outer layer of 3µm. After heat treatment, the required specification was readily achieved.

The full cycle of chromising by the rotary process followed by heat treatment was repeated some twenty times with satisfactory results both with regard to the metallographic structure and core hardness. All pins so processed were put through the barrel-finishing cycle to achieve the required final surface finish of R_z(max) 1.0µm and it was here that a problem was disclosed, namely, surface damage caused by impacting during rotation while being chromised. This has already been described as a problem with the old process specification and it was one that had to be overcome. It could not be ignored as in the past, yet the considerable advantages of the rotary process could not be sacrificed in favour of a box retort method.

Consideration of the textures of the new powder and the old showed there to be a substantial difference. While the new powder was finer in texture and therefore 'soft', the old powder with a larger particle size ferrochrome and also containing a more coarse alumino-silicate refractory was itself coarse and 'rough'. The cascading of pins down the exposed slope or angle of repose was somewhat slower in the new powder than with the old but in both cases the cascade was jerky as when a wave crest topples. This was caused by the drive of the gear train used to rotate the main tube of the furnace in which the retort was placed. This drive was of the indexing type, consisting of a toothed wheel and a pawl, the latter being lifted at intervals by an eccentric cam. Although the latter was continuously rotating, the effect on the retort was intermittent rotation hence the toppling wave crest effect. To achieve varying speeds of rotation an adjustment was made as to the number of teeth traversed by the pawl.

Experiments were made at slow and high speeds of rotation but the defect persisted although the incidence was lower at the slower speeds. Accordingly, it was decided to concentrate the mixing of the pins and powder in the early part of the process cycle before the system had become hot and then to reduce rotation to give long static periods. Some rotation was deemed not only desirable, but necessary, to prevent one of the problems of the static box retort process, namely sintering and shading of one pin by another where they touch. This new system, embodying the virtues of the rotary and box techniques, proved satisfactory and reduced surface damage to negligible proportions.

At this juncture, it was decided that the new process was giving a coating of the required morphology, and that it was also reproducible on an industrial scale. Thus Stage A had been completed. Work on Stage B, evaluating the coating performance had also been proceeding concurrently in laboratory trials. Rig tests had shown a reduction in both the first and second stages of the wear curves, bringing performance well within the targets set by the engine builders. Also, tests had been made on stationary test-bed engines with satisfactory results. It is further understood that diesel-engine cabs had the new chains fitted, this being considered the most arduous service to which one may submit an engine. The results, although interim, were very encouraging. Databases, of the performance of timing chains in engines have been built up over the years, including the wear performance, and therefore it is possible to assess how a new development is performing without waiting for ultimate failure, and this can lead to its earlier introduction into production engines. This was the technical/commercial decision in this project thus completing Stage B. Stage C is reported separately in Section 4.5.

4.4 Pre and post chromising processes.

At the time that this chromising process development was being carried out there was an almost inevitable over-spill of interest into the processes carried out on the pins before and after chromising. Reference has already been made(27) to a review of the older chromising process and changes were being already made to the ancillary aspects of the process when the work of this present report was started.

In the pre-chromising phase, the most notable activity was in the grinding operation. Here, one of the problems had been the forward feed progression through the centreless grinding. This led to a spiral defect. Also, there was evidence of a type of bounce or chattering of the stock on the horizontal support, which gave rise to an irregular pattern of flats, small, but visible to the naked eye. These problems were corrected by machine adjustments and also the installation of newer machines. Closer attention was also directed at the grinding coolant, and its cleaning, this being a re-circulating system of substantial volume.

What this brought about was not a major change of specification, but a closer tolerance band. The surface finish was still numerically as before, but there was an improvement in the quality of the surface.

Mention has been made earlier of the importance of storage conditions prior to chromising and this again was brought under tighter control as was the cleaning operation after grinding.

Mechanical damage was reduced by fitting rubber guards and chutes where parts were discharged from a machine or into storage trays.

Regarding post-chromising operations, these were conventional heat treatment followed by barrel finishing. The hardening was at 825°C in a controlled atmosphere (endothermic) followed by an oil quench while the tempering was in air at 240°C.

For barrel finishing there were the two options, one a conventional rotating unit into which pins, abrasive media and polishing compound were charged and left for a substantial period of many hours or, the preferred method of using a 'High-G' barrel. The latter consists of several small rotating barrels arranged in a planetary fashion at the ends of arms mounted on a central horizontal shaft. Pins, media and compound are placed in the closable barrels and when full and the machine is in balance the arms rotate as do the barrels on their ends so developing high 'g' forces on the load. This produces a marked increase in the grinding or polishing action and hence a reduction in process time. There was some concern at the pressures and impact effect upon the chromised coating and indeed some damage did occur. However, attention to the media and machine settings overcame the problem.

The final operation was to wash off any polishing media, rinsing in hot water and finishing in a heated centrifugal spin dryer.

Despite the amount of care exercised both in the various processes and in the handling between them, the small size of the pins necessitates some bulk handling techniques and the most vulnerable part of the pin is the shoulder at the ends. This is given a generous radius from cropping and rolling but nonetheless the coating suffers damage over this area and small pits are visible to the naked eye where coating has been partially removed. Fortunately, this area plays no part in the function of the pin and can be ignored.

4.5 Examination of new coating

4.5.1. General Microstructure and Growth

In Table 1., there is set out the results of analysis of three coatings each produced by different but broadly similar means. That identified as 'A' were the set of results produced by the engine builder and already discussed in Section 3.1. It is not known by what precise means the data was obtained except that it was via an electron probe micro-analyser using a conventionally mounted transverse section of a coated pin.

The group of results identified as 'B' were from a coated pin produced in the course of this work by the static box retort method while those of 'C' were from a coated pin produced in a rotating retort.

It will be seen there is doubt on the validity of some of the carbon and nitrogen values this being due to their being of low atomic number and the capacity of the equipment used. However, the generally lower chromium and higher iron values in 'B' and 'C' compared with 'A' confirm the observation in Section 3.1 that the pins of 'A' were processed in a compound based upon pure chromium.

Additionally, it can be seen that the ratio of the thickness of the outer layer to the whole is lower in 'A' than 'B' and 'C', although the total thickness of 'A' is 13µm with the 16µm for 'B' and 20µm for 'C'.

This led to a small experiment to determine when, and at what rate the outer layer grows. For this, small box retorts were made, of outer dimensions, 50mm cube in order to have high rates of heating and cooling. A small quantity of pins and powder was placed in a furnace at 1000°C which was being slowly flushed through with a gas mixture of 95% nitrogen and 5% hydrogen. This was to reduce the possibility of oxidation. The boxes were withdrawn at intervals of 3, 5, 7 and 9 hours after loading. Pins from each were transverse sectioned, mounted etc, and examined. All were found to have a three-fold coating and the results are shown graphically in Fig. 25. It is quite clear that the relationship of the outer layer being approximately 20% of the total layer thickness is quickly established during the process cycle and is maintained. Also, the two inner layers establish and maintain parity with each other regarding their respective thickness.

To date, many hundreds of metallographic sections of coated pins have been examined in the course of production control, and, in all cases, these relationships have been maintained. Of course, all pins had been through the full process cycle with no curtailment and were therefore about 15µm coating thickness.

Chen(18), although chromising with a fluidised bed and working with the high alloy steels D2, M2 and H13, noted the development of $(Cr.Fe)_2N$ overlying $M_{23}C_6$ carbide after processing for only two hours at 1050°C. This continued to thicken but no data was given as to its ultimate development and the photomicrographs do not distinguish it either. The only indication as to the final thickness of this nitride layer comes from the element distribution profiles. These show nitrogen falling from about 8% at the surface to effectively 0% at 3-5µm. The total coating thicknesses were 20-25µm. However, the given carbon value over the outermost part of the coating, coincident with the nitrogen, is 20% (approximately), falling to about 5%. Chen rightly makes the point that, since dry argon was used as the fluidising gas, the nitrogen must have come from the 2% ammonium chloride added to the chromising powder. However the analytical data given must cast doubt upon the claim that the outer layer is simply M_2N.

Fig. 26 shows an etched section through a three-layer coating and is typical of those produced over a period of time by the rotary process and the newly formulated powder. It is at high magnification, but shows quite clearly the zones which have resulted in it being termed a 'three-fold coating', and the three zones are so called in discussion, the outer, middle and inner layers. This particular illustration has been used because it shows in one small area many of the features which have been observed across a wide range of micro-sections.

The columnar structure is clearly visible, not only in the bulk carbide where it occupies a substantial area, but also in the outer layer where there is an indication of nucleation on a very fine grain carbide substrate. To some extent, this is reflected in the columnar grain size within the bulk carbide. There is also a small amount of spherical porosity which may be Kirkendall in origin but could be caused by the bridging over, by lateral diffusion, of a discontinuity in the deposition of chromium. The general rounding off of these cavities, making them appear almost as gas bubbles, could be attributed to the effect of surface tension and creep at the process temperature.

Within the surface of the outer layer there can be seen two grey areas. Although these were not identified directly by analysis, they are small particles of alumina from the compound which have become embedded, but not encapsulated, by the outward growth of the coating. One particle is showing the hexagonal ideomorphic form of alumina.

Near the interface of the carbidic zone with the substrate steel (white but with the acicular martensitic structure just visible), and 1-2µm from it, is a line of very small cavities or even smaller inclusions. This is very probably the original surface of the steel pin. It shows that the coating is very much one of growth. Also generating from this interface, are two small radial cracks which have healed over at the start of the columnar zone. Although a very large proportion of the atomic/ionic movement is radial or normal to the original surface, there is, nevertheless, sufficient lateral diffusion to bring about healing of some discontinuities. The coatings at room temperature are in compression and because of their crystalline stability, may be in compression at the process temperature, which would aid the healing mechanism.

The hardness values of the three zones are: -

Outer layer	1500 - 1600	$HV_{0.025}$
Middle layer	~ 2000	$HV_{0.025}$
Inner layer	~ 2000	$HV_{0.025}$

These values are in reasonable agreement with those given in the literature and serve to emphasise the distinctive characteristics of the three zones - certainly the outer layer from the other two. However, there is one important difference between the results given here and those reported by other workers in this field(23,24), namely the inversion of the hardness gradient from outer to inner zones of the coatings.

The diametric changes of the pin as a result of chromising are very important and significant. Important because of the engineering design requirements for assembly and subsequent performance in service and significant because of what they reveal about the mechanism of the chromising process. In practice there must be some degree of tolerance and here the procedure is to calculate backwards from the finished or final assembly tolerances to those of the pin before chromising.

After chromising, the pin diameter must be 3.320 to 3.325mm i.e. a tolerance of 5µm. Numerous measurements of dimensional changes showed that the increase of diameter of the pin as a result of chromising, heat treatment and barrel finishing was of the order of 20-25µm, which taking a mean of 22µm, shows there is a radial growth of about 11µm with a total coating thickness of 15µm. In other words, there is a penetration of the chromium diffusion into the substrate of about 4µm, the remaining 11µm being the growth. Within reasonable limits, given the experimental problems of what has been more of a statistical exercise than direct measurement of coating growth, these results go some way to support the view that, in Fig. 26, the small row of dark 'inclusions' mentioned above are, in fact, at the original surface of the steel pin.

4.5.2. Attempts at Phase Identification

Although it could be claimed that the coating as shown in Fig. 26 was to all intents as required by the engine builder and practical trials had shown it to be consistently superior to earlier coatings, there was no firm opinion as to what the constituent phases were. Literature already quoted(23,24) and upon which some comments have been made pointing out inconsistencies, suggests that the outer layer should be Cr_2N, the middle layer $M_{23}C_6$ and the inner M_7C_3.

Morphologically and structurally, the outer layer, with a thickness of about 3µm, looks quite distinct from the bulk of the coating with a quite definite boundary or interface. It has also been shown that, throughout the chromising process, it has a separate existence, growing at a consistent rate and not appearing to change its constitution although it is moving outwards from the original metal surface.

Accordingly, some attempts were made to determine the constitution of the three parts or layers of the coating, with the first being electron-probe micro-analysis (E.P.M.A.). Some of the results have already been given in Table I, and with the process being firmly established as using low carbon ferrochrome in a rotating retort, it is coating 'C' of Table I upon which the further work was concentrated.

A practical problem at this stage was the fact that within the company laboratories where the work was being carried out, there were no facilities for E.P.M.A. and other physical methods of analysis such as X-ray diffraction (X.R.D.). Because of this, and also working in both Germany and the U.K., it was necessary to use the services of consultant and university laboratories on a contract hire basis. This was not a good state of affairs and there is little doubt that some confusion of direction developed within this area of the investigation.

In Table IV are given the results of a series of E.P.M.A. analyses. They were carried out on more than one type of instrument and in different laboratories. Some of these results arose when in fact the purpose of the analysis was to determine the origin of occluded slag and other types of defect but nonetheless they were considered of sufficient validity at the time. It was the composition of the outer layer that was of most interest because it was half of the bearing couple formed by the pin and bush within the chain and also there were strong indications, indeed firm statements, in the literature, that the layer should or would be, a nitride of the form M_2N. 'M' would be predominantly chromium, and in some statements the outer layer was referred to as 'chromium nitride'.

Therefore, looking at the results given in Table IV, and recognising that the determination of the lower numbered elements carbon and nitrogen is not of the highest accuracy, it was disturbing to find that, although carbon was always present, nitrogen could vary considerably without there being any variation in the morphology of the coating.

The next stage was to see if X.R.D. would throw any light upon the situation and three attempts were made with this technique.

The first, in Germany, was both broad and in depth. A total of twelve specimens were examined, being taken from pins processed by the static and rotating processes and also using both low and high carbon ferrochrome. The coating morphology with comment is given in Table III, and this shows clearly the significant difference between coatings obtained using low carbon and high carbon ferrochrome. Fig. 29 illustrates the physical differences of the two types of coating. In Fig. 29(a) the layers are quite clear, while in Fig. 29(b) there is only one layer. What is common to both however, is the 2-3µm innermost part which it has been suggested delineates the position of the original surface. Also clearly visible is the columnar structure and nominal grain size of the coatings and how, particularly in Fig. 29(a), there is almost a new growth starting at each layer.

However, the X.R.D. results, obtained by reducing the coating to powder did not reveal any layer differentiation nor a difference between the coatings obtained using the two types of ferrochrome. In all cases the constitution of the coatings was reported as: -

Cr_7C_3	ca. 100%
$Cr_{23}C_6$	≤ 5%

No comment was made regarding the 'chromium' as being a mix of iron and chromium neither was comment made on the possible lattice distortion which occurs when iron replaces chromium in the carbides.

Some further X.R.D. done at Cambridge and this time working on the coating itself as opposed to a powdered sample, and concentrating on the outer layer, indicated that it was 'predominantly $Fe_{20}C_9$ with the possibility of there being some Fe_7C_3'. This was stated along with E.D.X analyses of the coating showing *Cr:Fe* ratios of 7:2 falling to 12:7.

Another attempt at resolving the problem was made at Loughborough using specimens similar to 'A' in Table III, i.e. pieces of strip of the same composition as the chain pins. Here the incident X-ray beam was normal to the surface as opposed to the glancing angle used by Cambridge. The results were not clear and could only be expressed as the outer layer being probably $M_{23}C_6$.

In addition to the X.R.D. described above, there were many E.P.M.A. measurements made on various parts of the coating the object of much of this work being the determination of origin of defects such as slag inclusions etc. As noted earlier, the values for nitrogen and carbon need to be treated with caution but nevertheless, nitrogen was always found at up to 9% by weight, decreasing from outside to inside. The corresponding carbon values were always higher than the nitrogen by 2-4% by weight when measured at the same point in the coating.

5. FURTHER DEVELOPMENTS

5.1 The quality of raw materials

It has been noted earlier in Section 2.6.1. that the source of chromium used in chromising can be of considerable importance. The simple ratio of chromium to iron is not sufficient and safeguards have to be incorporated regarding quality which would not be necessary if the ferrochrome were being used directly as an alloy addition for steel-making.

Although in the experimental and early production work with the new coating, the 70:30 ferrochrome was being purchased from a reputable supplier, some evidence of slag melting onto or adhering to the surface of the chromised pins was found. The situation became critical however when a quantity of ferrochrome was bought from another supplier. It was nominally of the correct specification but produced chromised coatings which were contaminated by a quite unacceptable amount of slag. This led to an in-depth examination of the manufacturing process of the ferrochrome and various special checks were incorporated over and above those already in place.

In the silico-thermic process, that is (b) in Section 2.6.1., the principle is for the active slag to float on top of the molten ferrochrome when it is poured into open slab moulds. Further, it is so constituted that on cooling, the slag breaks down into a friable powder which can be almost brushed off.

Although this happens as described, nevertheless, some slag is trapped in the solidifying metal. When the large slab is broken for crushing, it is possible to see the very dark slag against the silvery fracture faces of the ferrochrome, and this allows some hand sorting to be carried out. By putting this practice in place and using the percentage of oxygen as a guide to its effectiveness, it was possible to not only improve the quality of the ferrochrome but also to reduce the incidence of slag induced defects on the chromised pins down to a tolerable level.

It is unlikely that the chromising process will ever be totally free of the problem unless recourse is made to pure electrolytic chromium, but this is much more expensive and thus a cost/performance balance had to be made. The development of a special 'in-house' quality procedure with one ferrochrome producer also ties one with regard to purchasing power, but again, the situation is tolerable.

Regarding the alumina used, there are available in powder form two types, calcined and fused. The former, because of its method of manufacture, has a relatively narrow band of grain size available while the latter can be purchased over a wider spectrum. Both are >99.5% Al_2O_3 and very low, <0.05%, in Na_2O, SiO_2, and Fe_2O_3. Historically, both types have been used in the formulation of metal diffusion powders the reasons for particular choice often obscure or because of some perceived advantage such as 'flowability'.

In the work reported here, calcined alumina had been used in the earlier process and its use was continued with the new process. However, there developed outbreaks of a defect which can best be described as a 'scab'. The chromising *per se* was satisfactory but the outer layer of the coating contained a very high proportion of occluded alumina and a cross section through the defect is shown in Fig. 27. To the naked eye, the surface of the pin was dull and lacked the normal metallic sheen. Within a given batch of 80 kg of pins, up to 20% could be rejected for the defect.

Examination of production records showed only one significant variable which was the use of a new consignment of calcined alumina. This had been produced in ostensibly the same manner and on the same equipment as previous supplies. Traceability was unquestionable. Detailed examination by chemical analysis, X-ray diffraction, Thermal Gravimetric Analysis etc. showed no differences between 'good' and 'bad' powder. The evidence of the metallographic examination of the rejected pins showed that the particle size of the occluded alumina was 1-5µm and tending to make the coating thicker than normal i.e. 20µm instead of 15µm hence the use of the term 'scab' as a graphic description.

What other variable of the process, triggered an unidentified variable in the calcined alumina is impossible to say, but the outbreak lead to the use of crushed fused alumina of mesh size 0.177-0.250mm thereby removing the lower size fractions found naturally in calcined alumina.

Perhaps the best explanation of the calcined alumina problem can be gained from Fig. 28 which shows the structure of calcined alumina. The idiomorphic hexagonal structure is clearly visible but more importantly the sintered or conglomerate nature of the larger particles. They are in fact made up of particles ranging from submicron to about 30µm and they appear friable with an easy cleavage. The chromising process involves some rotation and hence comminution which could cause a higher proportion of fines to develop. This is only a working hypothesis which has not been pursued further because the use of fused alumina substantially resolved the problem.

However, it is unlikely that coatings will ever be completely free of some inclusions of refractory of micron or sub-micron size because such particles will develop as a result of mechanical and possible thermal fragmentation of larger mesh sizes. The removal of 'ultra' fines has been considered using air elutriation but rejected for now on the grounds of cost but it seems the only likely technique.

5.2 Process development and control

Apart from the problems of quality described earlier in Section 4.2 which relate to the older rotary process and which can be attributed to raw materials or of mechanical origin, there were no defects which could be directly attributed to the new process. However, there were procedures within the inherited production cycle which warranted attention either from a quality or cost aspect.

The practice of exhausting the air from the closed retort and back-filling, with the 95% nitrogen, 5% hydrogen, 'formieren' gas, while appearing to be sound practice, had never been validated and recorded. Also, because the gas contained elements which form ammonia, and because this gas features in the chromising reactions, together with the indications that nitrogen had some influence on the formation of the third or outer layer of the new coating, it was deemed necessary to investigate the vacuum practice more fully.

In the early stages of development of the process it was carried out in rectangular steel boxes using fusible glass seals. It was static and no attempt was made to exhaust the interstitial air in the powder and substitute nitrogen. However, the results regarding the development of the three layer coating were as hoped for and therefore there did not appear to be a need for removing the air before processing.

Obviously, the air may have an effect but it is a question as to its significance on the process and, most importantly, on the final product. The sequence of events on the heating of the charge has already been described in Section 2.4 where the volatilisation of the ammonium chloride pushes the air out of the container or retort before chromising begins. This is at about 550°C but at different times in different parts of the container and a clean steel surface will oxidise at temperatures above 200°C and quite rapidly at 450°C. Also, the fresh ferrochrome added to the powder, with its high surface area to weight ratio, will readily pick up oxygen before 550°C, so that the interstitial atmosphere within the powder is very probably almost entirely nitrogen when the ammonium chloride volatilises. Thus, if this degree of oxidation of the charge can be tolerated, then the prior vacuum exhaustion seems unnecessary.

Following this reasoning, trials were made with the rotating retorts in which the vacuum exhaustion was omitted and the results were quite normal. The pressure in the retort steadily builds up to between 3 and 5 atmospheres at which point the pressure relief valves open to exhaust and as the process continues so the pressure gradually decreases such that at the end of the cycle of 7.5 hours at 980°C (furnace temperature), it has fallen back to 1½-2 atmospheres above ambient.

Some further trials were made in which the pressure relief valve was set at just above atmospheric and again the results were satisfactory with no post-chromising oxidation as a result of air being sucked in on cooling. When cool enough to open the retort at about 50°C allowing ingress of air, there is, of course, no problem with oxidation.

It was decided to maintain the pressure control at up to 5 atmospheres for two reasons. Firstly, as an insurance against the possible ingress of air and the fact that it is an operational check on the head seals of the retort. Ingress of air may cause an explosion. Secondly, it could help to stabilise the shape of the retorts operating at up to 1000°C, although this is a marginal factor.

The adjustment of the time cycle to 7½ hours from time of charging the retort into a hot furnace to discharge, is to allow three shift working. Such adjustment can be made by balancing against the process temperature. Further, the slow rotation of the retort gives a much better heat distribution in the charge of powder and pins compared with the static box retorts.

In the early process and also when processing pins in the rectangular retorts the ratio of weight of pins to weight of compound was approximately 1:1. In fact it has been an almost traditional value within the diffusion chromising industry, certainly as a yardstick by which to start processing a new part until production data allows a change. Therefore, as data was accumulated in terms of reproducibility of the required coating, its surface quality, and chemical composition changes within the powder, so the parts:powder ratio was modified to maximise the yield per process cycle and was finally stabilised at almost 8:7 by weight.

Concurrent with establishing this ratio was the balancing of the regeneration rate of the powder after each process cycle. This was eventually confirmed at 10% by weight of a 50:50 mixture of 70% ferrochrome and fused alumina powder thus maintaining a chemical composition of about 35% chromium and 15% iron. The residual chloride content of the powder after use is between 0.5 and 0.7% and to this is added 2% fresh ammonium chloride on regeneration. This is a relatively high regeneration rate but it is justified when using an open textured powder and, what is more significant, in a process where the charge is moving. The rate of heating is high, and the volatilisation of the halide over a relatively short period of time, makes an excellent contribution to expelling any residual oxygen, before the actual chromising commences.

5.3 Examination of the bush

Although the primary area of work in this project is the pin, as has been pointed out earlier in Section 3.2, the pin is only half of the wear couple, and it was inevitable that the inside of the bush, in which the pin part rotates, should be looked at. To pursue this, some chains with varying lengths of service were dismantled, the bushes removed from the link plate and carefully cut open, longitudinally but at right angles to the line of contact with the pin.

Obviously, the bushes from long service chains showed a greater area of polish thus corresponding with the two areas of wear towards the ends of the pins. However, what was significant was the area around the polished zone at which contact was starting. This showed very small rubbed areas of micron size and evenly spaced. Examination of the inner face which had not been worn showed a definite 'orange peel' effect, albeit very fine, but nonetheless present. This effect is common in cold-worked metals and is a manifestation of grain-rolling, during forming, where there is no surface ironing as experienced when actual drawing, takes place.

The making of the bush has been described in Section 3.2 and the primary area of surface planishing is on the outside face due to the roll forming. At best, the inside face is simply pushed hard against the mandrel.

With micro-sections prepared of a range of bushes, it became evident that the severity of the 'orange peel' was proportional to the grain size of the steel strip used in their manufacture. The finest grain found was about A.S.T.M 12 while some was as coarse as A.S.T.M. 4. This represents an average grain size of 0.00003 sq.mm compared with 0.0078 sq.mm which is a very wide variation. Put another way, it is the difference between 32,800 and 120 grains per sq.mm. Thus the roughness of the bore of the bush, which is in compression during forming, will be much greater with the coarse grain than the fine. Although the science of wear, friction and lubrication is complex(28) and difficult to quantify, it is clear that the wear rate of the coarse grain material will be greater than that of the fine grain, under the same operating conditions. Therefore specifications were modified, albeit as a compromise with the steel suppliers, to put a maximum of A.S.T.M 6 for the raw material, En 10084. This is nitro-carburised, hardened and tempered to a surface harness of 700 min. D.P.N.

Experience to date shows that the closer control of grain size, although not as precise as intended, has made a very useful contribution to improving the wear characteristics of the chain.

A further improvement relates to the positioning of the bush in relation to the link plate. From the roll-forming of the bush out of a cropped length of strip, there is a longitudinal join line where the two ends abut. Although as much care as possible is built into the manufacturing operation, it is inevitable that in such a high speed manipulative process, with materials having properties within a specification range, there will be variations, however slight, in the bush geometry at the join. The most likely is that the diameter of the bush can be somewhat 'pear-shaped'. In an ideal situation, it would be best if the location of the join were to face the inside of the link allowing the pin to bear against a uniform surface.

The chain components are assembled automatically and the position of the bush was at random in relation to the link but it was recognised that the reasoning above was of sufficient merit to warrant close consideration. As a result work was put in hand to automatically sort the bushes, orientate them and feed them, so that on assembly the join was on the inside of the link and out of critical contact with the pin.

6. SUMMARISING DISCUSSION

6.1 The chain bearing

Reference has been made to the classic book on friction and lubrication by Bowden and Tabor(28), and although first published in 1950 its contents are still valid today. Although the number of variables in a bearing is relatively small their interaction is complex and it is very difficult to change one without it having a 'knock-on' effect.

Fortunately, in the present work most factors are stabilised. The lubrication, the temperature and the nature of the loads being transmitted are known or at least are consistent wherever the chain product is being used. A given chain is intended for a certain type of engine which in turn is to provide a given service in a vehicle. Misuse is well recognised as a fact in performance but by and large there is a broad band of normal usage by which or in which a chain can be judged as to its performance. That performance is centred largely on the behaviour of the pin and bush.

For many years now within the realm of transmission engineering, there has been and there probably still is, a belief that, if one wants a bearing to last longer it should be made harder and there is a lot of practical experience to support this idea. The development of the C.V.D. and P.V.D. technologies enabled hardness values of 1500 D.P.N. and much higher to be achieved on a regular production basis. In fact, the project reported here is dealing with a C.V.D. coating of 1500 min D.P.N. However, it is operating against a significantly lower hardness below 1000 D.P.N. There is an important difference in that the material providing the lower value hardness of the bush is a hardened nitro-carburised carbon steel possessing a somewhat different lattice structure from that of the chromised pin. This difference in structure is also recognised as a commendable property in a bearing couple because it can reduce the amount of wear by reducing the welding tendency between asperities.

This welding tendency is, *inter alia*, also affected by the applied load on and in the bearing and where asperities (i.e. roughness) exist, they will be carrying the load and hence the actual loads within the peak of the asperity can be very high. This causes welding by friction and a tearing out of the surface of the bearing material. From this it follows that improving the surface finish of the bearing couple must be an advantage because it is spreading the applied load over a larger area and thereby reducing the unit surface stress. Another aspect of this same concept is to have on one of the bearing faces a material which can wear down quickly to give the smoother face prior to the harder materials of the longer term bearing coming into play. This is the general idea with the white metal and bronze bearing shells favoured in the heavy engineering industry.

The reason for this very condensed version of bearing technology is because there appears to be a conceptual problem as to why and how this whole project was conceived.

It will be recalled that the original proposition from the engine builder was that some chains had performed better than others under like conditions of service. The only criterion available was that they lasted longer i.e. showed less wear. Examination of the pins only (?) revealed they were made from a medium/higher carbon steel which had been chromised but the coating showed an outer layer of about 3µm which was not seen on other chromised pins. Analysis of the outer layer suggested that it contained nitrogen. The evidence presented was a photomicrograph and the small amount of analytical data with the request or question as to whether it could be reproduced on a production basis. There is little doubt that, in the minds of the engine builders, the presence of nitrogen was of the highest significance and it was producing a nitride outer layer, although no X.R.D. examination had been made to support this view. Neither were hardness values given which, if higher than those of the underlying carbide of the coating, would suggest a nitride or at least perhaps a complex of inter-metallics.

From the original photomicrographs there was no doubt there was a distinct outer layer of about 3 microns overlying the remaining 12µm of the 15µm coating. This outer layer is not differentiated using the traditional ferrous etchants such as Nital and Marble's reagent except rather vaguely but shows up well with Murakami's reagent. This reagent, an alkaline ferricyanide, is normally used to distinguish between carbides and nitrides in which the carbides are darkened while the nitrides remain unchanged. Chromium carbides are said to darken along with certain tungstides(29). Although in this particular case the inner chromium rich carbides do not darken appreciably, they are differentiated from the outer layer, and it could be that it is from this effect that the outer layer was thought to be a nitride. When nitrogen was found in that layer, irrespective of the fact that there was as much or more carbon, the hypothesis was confirmed that it was in fact a nitride - or so it seemed. There was much emphasis put upon the concept of a three layer coating and providing it was produced by a chromising process, the nature of these three layers seemed rather vague, except that the outer should be a nitride. A particular structural form was, so to speak, the requirement.

Initially within the development group it was accepted that the outer layer was a nitride, this overlaying mixed chromium/iron carbides. There was sufficient evidence in the literature to indicate that, if certain formulations of powder and process were followed, then an outer layer of nitride would be obtained. Also, direct past experience had shown that nitrides were a possibility in certain chromising processes.

With the in-house experience of chromising available, the direction of the work was not difficult. The compound formulation was evolved in small static boxes and showed that the required structure could be achieved. Due consideration of the process techniques available pointed to the rotary retort as the most suitable, again, in part, because there was in-house experience. There were some problems in translating from the 'static' to the 'dynamic' method but these were steadily overcome without sacrificing the structural integrity of the coating. With time, defects were reduced to what was considered an acceptable percentage of throughputs.

The chain performances on test-rigs and in engines was as required, in fact, probably more so and that could have been considered the end of the project. However, this was not so, because it seems inevitable in technology that one cannot avoid looking at other issues alongside the main line of enquiry. In this particular case, it was to apply some of the basic concepts of wear theory to the bush/pin couple. The pin had ostensibly been improved with a more wear resistant coating and concurrent with that development, attention was paid to the inside of the bush. As has been described in Section 5.3, this is probably the most difficult member of the wear couple because of its accessibility or rather lack of it. Because there could be no increase in costs there could be no extra operations and therefore internal bore finishing, although tried, was discounted. It was because of this situation that attention was paid to the behaviour of the steel strip and the realisation that the raw material grain size was having a substantial effect on the surface finish and hence the wear characteristics. Also, the consistent positioning of the edge join in the bush away from the pin made a further useful contribution to chain life.

Thus, it can be said that the undoubted improvement in the chain performance which has been obtained came not from one source but from several. There were some major contributors such as the three-layer chromised coating which is described in this thesis but there were others, such as a focusing of attention on avoidable defects and improving factory operators' awareness of the significance of what they were doing.

6.2 A comparison of the new and old coatings.

As has been established, the new coating consists of three layers, and this has been achieved by using a low-carbon ferrochrome as the source of chromium. The 'old' or previous coating was a mono-layer of carbide and to produce this, a high carbon ferrochrome was used. Whatever the constitutional differences may be between the two types of coating, their structural differences are clearly shown in Fig. 29(a) and (b).

Both have a zone of mixed crystals at the junction with the base material and of approximately the same thickness namely 2-3µm. The crystallite size is also similar, perhaps somewhat finer with the old coating. The old coating then develops a classic columnar structure, virtually unbroken to the surface, a distance of some 10-11µm. The cross-sectional area of the individual columnar grains is similar to that of the grains or crystals on which they generate. Thus there is a coating made up of hard crystals of very high slenderness ratio.

By contrast, in the new coating, although the crystal growth is again columnar it appears to be less continuous with many transverse fractures and also there are the two major horizontal planes. There is virtually a complete change of nucleation at these planes and the outer layer of some 3µm thickness has a much more equiaxed appearance not unlike the innermost layer of 2µm. It is important to note the correlation of structure between that shown in Fig. 29(a) and Fig. 26.

6.3 Consideration of other coatings

When it became apparent that the three layer coating showed a substantial improvement in performance over the older mono-layer and, that at that time, the belief was that it was due to a nitride of chromium, it is not a big step to consider a chromium nitride coating *per se*. Accordingly, sample pins were processed by Tecvac Ltd of Cambridge using a P.V.D. process they had developed whereby chromium is vapourised by an electron beam in an atmosphere containing nitrogen which condenses on the target to form chromium nitride. As with many P.V.D. coatings, it is typically a line-of-sight type and thin at about 3-4µm.

To procure a fair comparison with the chromised coating, the pins were made slightly oversize so that the final 'as-coated' diameter was according to specification. Also, the pins were placed end on in a special jig similar to a mushroom head so that all surfaces could be 'seen' by the stream of chromium ions emanating from the target. Sections of the pin showed the coating to be even around the circumference.

When coated, the pins had a bright appearance and the surface was within specification but there felt a slight 'grittiness' so that a very light barrel polish was applied. The hardness of the coating (given as CrN) is about 2000 V.P.N. but this overlies a layer of chromium of approximately 1µm thick.

The results of laboratory life tests using both a rocking link and an assembled chain showed that the bedding-in period was satisfactorily short and the slope of steady state wear acceptable but no better than the three layer coating. Further, because the coating was thin, it wore through before any meaningful life data could be determined. Additionally, the process costs were much too high and so the project was abandoned.

A further process to be considered was that developed by Teer Coatings Ltd of Kidderminster. This consists of a rotating barrel inside which is a sputter ion plating system targeting the bottom inside of the barrel where the charge is placed. This system overcomes the problem of line-of-sight methods as the charge is agitated by the rotation of the barrel. Again it is possible to coat with *CrN* and also MoS_2, the latter being well known for its low coefficient of friction.

For these trials, similar provisions were also made as with Tecvac with regard to dimensions and again the coatings were 3µm thick. The MoS_2 coating is only 1µm but overlying 3µm of *CrN*.

The same laboratory life tests were carried out as with the *CrN* from Tecvac and similar results obtained but once again the very high process costs prohibited any further consideration.

It is difficult to say what was learned from this exercise (except the high cost). The shape of the nose of the life test curves of these two other coatings was no improvement on the three-layer chromised coating. It was in between the curves shown in Fig. 18, indicating more 'bedding-in' and neither was the steady state any flatter which would have suggested a better wear rate.

6.4 Why is the new coating effective?

The concept that the problem as presented by the engine builder was a dual one has been mentioned several times in this thesis. Basically it is one of improving the wear resistance of the pin/bush couple which it was thought could be achieved by applying a new type of chromised coating. The only way of measuring the success or otherwise of the whole project was based on the results of wear tests. There was no other way. Chemical compositions, hardness values and crystallographic data are, of course, helpful in the development programme, but they give little real guidance when it comes to wear phenomenon.

It is important to realise that the thickness of the coating has not been increased, only its constitution has been changed, and this has brought about the reported improvement in performance.

Comment has been made earlier that other aspects of the chain manufacturing process have been improved in a way concurrent with the introduction of the new process. It has been recognised that these have made a very useful contribution to the overall improvement in chain life. However, none of these changes had been implemented when the first trials were made of the modified chromising process. These were done in small laboratory units before scaling up small industrial size retorts and before developing the rotary furnace adaptation. It was the pins from these early trials which were heat-treated and barrel finished by the then standard procedures, which proved that the modified coating was conferring the much improved life when compared with the then standard chain. Neither were these good results chance effects, because at each stage of process development, wear tests of one type or another were carried out - they were the criterion, not a specific microstructure in a chromised coating - that was only a guide.

As tonnage throughput was achieved with consistent good performance figures, attention naturally turned to the question as to why the new coating should be as good as it was proving to be. The results of various tests, analyses, etc. have been reported in earlier sections, and they are, in fact, only part of the sum total, included to illustrate a particular aspect of the work involved.

It is true that, at first, based in particular on the work of Komen(23) and Tachikowski(24) it was thought that the outer layer was a nitride of the form Cr_2N. However, this could not be substantiated and there was always more carbon found than nitrogen, although there was always nitrogen present to a greater or lesser degree. Therefore, it was accepted, subject to a future confirmation, that the outer layer was a carbo-nitride of chromium with some iron. The results of analysis would only allow a general formula: -

$$(Cr.Fe.)_x\ (C.N.)_y$$

and it is recognised that this is somewhat vague.

However, it is difficult to see how one can be as precise as other workers have claimed to be when dealing with a diffusion process such as chromising where chemical compositions are changing rapidly over distances of a few microns. Certainly, there is no question of attaining anything like equilibrium, because it implies that, to all intents and purposes, diffusion had ceased and stoichiometry has been attained for the compounds.

Of the two major or common ternary carbides of chromium and iron, $M_{23}C_6$ contains about 5.3%C and M_7C_3 about 8.4% (by weight). Therefore, since when using low carbon ferrochrome, the supply of carbon comes from the substrate steel, it is reasonable to suppose that the $M_{23}C_6$ carbide will always overlay the M_7C_3, if both are resent. Also, by the same reasoning, if there is a nitride or carbo-nitride formed, because the nitrogen can only come from the chromising gaseous atmosphere, these nitrogen bearing phases must overlay the $M_{23}C_6$ and M_7C_3 *carbides*. Therefore, if the outer layer of the three-layer chromised coating is in fact a separate and distinct phase as it very much appears to be, then it must be a nitride or carbo-nitride type, and, as has been reasoned earlier, because carbon is always present in it, it must be the latter.

The carbo-nitrides in ferrous metallurgy are an ill-defined group and it is understood that X-ray crystallographic data is not reliable, in fact, it may be impossible to determine accurately. This may explain the confusion in what has been reported by other workers and the disagreement between laboratories which were used in this investigation.

However, reverting to the differences between the old and new coatings in the present work it is difficult to see why an $M_{23}C_6$ carbide should have a markedly different wear resistance from an M_7C_3 carbide. The hardness values given by Tackikowski(24) range from 1452-1975 H.V. and can apply to either carbide, yet Komen(23) claims a hardness of only 900 H.V.for M_7C_3. From past experiences(21), this latter is much too low for a carbidic chromised coating.

The focal point of the Hertzian stress in the coating is travelling at high speed in a lateral direction as viewed in Fig. 29. Its maximum is understood to be slightly below the actual surface and at this point, and indeed, in its immediate environs, there will be significant shear stresses operating at a high frequency and at an amplitude from zero or perhaps lower i.e. negative. In these circumstances, it is probable that the structure in Fig. 29(a) is better able to cope with this situation than that in Fig. 29(b). It is also probable that the structure is more able to cope with the much higher transient point stresses and temperatures during the 'bedding-in' of the pin/bush couple. This is suggested by the smaller 'nose' of the curve in Fig. 18.

Summarising, it seems quite feasible that the improved performance of the new coating has little to do with whether the outer phase is a nitride, carbo-nitride or carbide *per se* but more a question of morphology and an analysis of how this comes about is given in the Appendix.

6.5 Further investigations

These fall into two parts, namely (a) the process and (b) the coating.

Dealing with (a) first, as a general comment, diffusion processes involving the heating up from cold of a large mass and then letting it cool to room temperature is not thermally efficient and there are very few ways to get away from the problem. It is, in fact, a batch process involving as much or more non-productive weight than productive weight.

The plant carrying out the processing of chain pins has been doubled in size to cope with the increased demand and the time/temperature cycle has been fine-tuned to 7½ hours so that three cycles per furnace can be achieved each day and, with shift working, seven days per week. It will also be possible to obtain some waste heat recovery from the gas-fired furnace flues and by forced-draught cooling of the retorts when taken from the furnaces, but that is about all.

As a total departure from normal practice, a scheme was drawn up for using a scroll furnace. The furnace technology is known and as the process can be operated at a nominal atmospheric pressure that would not be a problem. Also, the powder and pins as a mixture, lend themselves to progression via a scroll.

However, there was/is an anxiety at committing what would be a substantial charge of materials in process at any one time. At present it is 82 kg per retort as opposed to about 1000 kg in a continuous process and this is considered too high a risk without a considerable development programme.

Regarding (b) the coating, reproducibility is not a problem with a throughput of several hundred tonnes per annum. Savings have been made in material sourcing but there have also been problems in this area. Therefore, with the product now widely accepted, there is not much incentive to make significant changes. In fact, customers would resist such a move unless further substantial gains could be shown. That is only in two areas, cost and performance.

On performance, there is the understanding of the coating and its relationship with the bush and this should start with a thorough physical and chemical analysis all more or less in one research laboratory, say a university. The somewhat piece-meal approach which, due to force of circumstances, is how the current investigation was carried out, obtained the desired result more by many years of experience and intuition rather than what might be termed classical research.

What is in mind, apart from clarifying the crystallographic problem, is the application of sophisticated techniques to an assessment of the mechanical properties of the coating. For example; can load/hardness curves help; can controlled bend tests with either acoustic or electrical resistance measurements be worthwhile? Would deformation under liquid with potentiostatic measurements yield information on cracking? Is it possible to effect controlled anodic dissolution of the coating to obtain a better understanding? These are the techniques which it is thought could throw further light on why and how the coating works. The main question however, is largely a commercial one not scientific. Do we really **need** to know, when production output has more than doubled, another factory has been purchased and the new chain is now the bench-mark against which others are judged?

7. CONCLUSIONS

A. The work centred on the reproduction of a specific metallurgical structure formed by chromising a carbon steel. This was identified as being a complex layer of chromium and iron carbides with possibly some nitrides.

B. The industrial chromising process necessary to reproduce the structure was found to be based on a powder compound, the metallic component of which must be either a low-carbon ferrochrome or pure chromium.

C. Two basic chromising processes were evaluated and one consisting of a rotating retort giving relative movement of parts and powder was developed. This gave a consistent coating which embodied the structural requirements referred to in (A).

D. Laboratory and engine trials of chain pins produced as in (C) showed a 50% reduction of wear in the initial stages of service and a substantial increase in the total life of the chain.

E. It was proven that the increase in life (decrease in wear) was attributable to the development of the 'three-layer' chromised coating on the chain pin and not to any other aspect of the finishing process.

F. Subsequent to the improvement gained by the three-layer chromised coating, further improvements were made in the chain assembly to give a fixed position of the join in the roller in relation to the pin.

G. It was shown that improved wear characteristics of the roller/pin couple could be obtained by reducing the grain size of the steel strip used to make the roller.

H. It was not possible to state with any degree of certainty what was the constitution of the outermost layer of the three-layer coating. It was not a simple nitride and its most likely constitution is that of a carbo-nitride of chromium with some iron. The carbon/nitrogen ratio was shown to be variable as was that of chromium and iron, but this did not detract from the ultimate performance of the three-layer coating.

I. It is proposed that the substantial improvements in wear properties are more to do with the specific morphology and crystal form of the coating than with its chemical composition.

APPENDIX

Some commercial observations

Any improvement in the performance or life of a component in the Automotive Industry is always welcome provided that it comes with the minimum cost penalty or better still, a saving. Indeed work is going on all the time among prime manufacturers and their suppliers to this one end. There are many examples of where a chance observation by someone who can interpret the event can be turned to advantage and the project reported here is one of them. Several observations can be made: -

(i) The work has centred on the reproduction of a specific metallurgical structure. That the basic process to be used was chromising and that the coating was carbidic because it was being used on a carbon steel was obvious at the start but the novelty was whether one could achieve a consistent product with the incorporation of nitrogen in the carbide coating. It was this that is thought to have given the improvement in the timing chain performance first observed by the Tribology Laboratory of the engine builder. There was the almost inevitable proviso that the new chain should not be any more expensive than the old one it would replace. Quality was also as important as cost.

(ii) Within the project team a considerable amount of experience of chromising and what had been going on in the industry as a whole, was also well known. Many other workers in the field had been known personally and others were still in contact and therefore the project could not be considered 'green field' science.

(iii) For these reasons, it was not necessary to start as it were, at the beginning, but rather assess the situation and choose the best options. This was done by devising a new powder formulation which was shown to give the desired results and then adapting that powder to the best process technique, namely the rotary retort. Again, satisfactory results were achieved in terms of chain performance, but not without a fair amount of selection of raw materials.

(iv) As has been noted in the preceding sections, although the project could be adjudged to have been brought to a successful conclusion it was not **really** known why the new coating should be superior to the old. The structure of the new coating was consistent over many tonnes of throughput and it had been eagerly accepted by the engine builder as a break-through in overall engine performance. However, the old coating has also been consistent in properties but it was not as good as the new one.

(v) Examination of the literature relating to this area of chromising showed a marked lack of agreement and, as work on the constitution of the new coating got underway, so there developed a different thinking from that of previous workers as to the nature of the coating, and it is true to say that this difference of opinion still remains unresolved. Because of the general run-down of the chromising industry as applied to general engineering, it seems reasonable to say that, unless the chain manufacturer or manufacturers investigate the problem, it will not be resolved. The system developed as a result of this project works very well as it is, so why do further work? In fact, it is not in the interests of a chain manufacturer to publish how the coating is achieved, because it is very difficult to obtain a protective patent.

(vi) With more than 1,500 tonnes of pins now processed satisfactorily, and with millions of service miles on record, there has been little incentive to proceed further. Other types of expensive coating, similar in chemistry have been tried with no improvement at all.

(vii) Thus it has become a management decision, heavily influenced by commercial and financial factors as to whether the project will be taken to what is, in scientific terms, its logical conclusion. That decision, it seems, has not been made and is probably a long way away.

Some theoretical observations

The writing of this thesis has had a somewhat therapeutic effect because attention has been focused on the coating and its formation rather than its behaviour or performance though it is almost impossible to consider one aspect in isolation.

In the development work several observations were made which may throw some extra light on the chromising process itself and on the three layer coating in particular.

It has been shown than the outer layer is present almost at the start of chromising and it then grows proportionally with time in the same manner as the two inner layers. It has also been shown or at least there appears strong evidence to support the view that, from the original specimen surface, there is a modest amount (~2µm) of inward diffusion of the chromium/iron carbide. In other words, much of the coating is growth. See Fig. 30.

Because the outer layer is present very early in the process, it is not unreasonable to suggest that, in relation to the chromising atmosphere generated by the low-carbon ferrochrome, this outer phase or constituent is perhaps the equilibrium surface of the process. All the chromium which goes to make up the bulk of the coating must pass through it - there is no other way. Therefore the outer layer is in a continuous state of flux, yet it still maintains its integrity and indeed grows. Some of that growth is the chromium passing through, some is iron either from the substrate or perhaps more probably from the ferrochrome itself. The remaining constituents are carbon and nitrogen. The latter can only come from the chromising atmosphere, either from the ammonium chloride or from air within the retort. The carbon has two possible sources, namely the ferrochrome and/or the substrate steel of the specimen or component. If a low-carbon ferrochrome is being used, then the source of the carbon is the steel, but if a high-carbon ferrochrome is used, the source can be and probably is both i.e. steel and processing powder.

It has been established that the old coating obtained with high-carbon ferrochrome has no outer layer (see Fig. 29(b)) although again, it is reasonable to suppose there would be just as much nitrogen present in the chromising atmosphere as in the case of the low-carbon ferrochrome powder. Yet, in one case nitrogen is not absorbed and in the other it is.

The probable answer therefore, lies in the carburising potential of the chromising atmosphere. If it is high, then no outer layer is formed. It could almost be said that when the outer layer is formed, it is perhaps the very first thing to be formed, and the chromium is being laid down at such a rate that there is insufficient carbon moving up from the substrate and so the chromium combines with the nitrogen; after all, chromium is recognised as a strong nitride former. The rate of supply of carbon to the surface is governed by four factors: -

i. the percentage composition in the substrate steel i.e. the carbon gradient,
ii. its rate of diffusion through the substrate to the active interface and this, *inter alia,* is a function of what carbide stabilizers may be present,
iii. its rate of diffusion through the carbide layer as soon as the latter is formed,
iv. the temperature.

It can also be argued that the rate of decarburising at the outer surface is a controlling factor and this is true but of less significance with the high carbon steels than the low carbon type.

Summarising, it seems quite possible to form nitrides at the surface under certain circumstances and several experimental methods suggest themselves to create 'abnormal' conditions to test this idea. However, if carbon is present, then irrespective of where it comes from, it will interfere with the formation of nitrides as such and create carbo-nitrides of varying ratios of $C:N$. In diffusion processes true stoichiometry is probably impossible to achieve and one will always have phases or compounds whose composition is variable as is the 'M' in $M_{23}C_6$ or non-stoichiometric as in, say $TiC_{0.9}N_{1.1}$

Equilibrium is attained in infinite time and industry has neither the finance nor the patience to justify such ideality!

	Zone	Thickness in micron	% (by weight) Chemical Composition			
			C	*Cr*	*Fe*	*N*
Coating 'A' original ex engine builder	outer	1-2	6	88	~0.8	2-5
	middle	~5	12	87	4	-
	inner	~6	11	55-60	32-38	
Coating 'B' using low carbon ferrochrome and static retort	outer	~3	?	71	15	?
	middle	~7	13	71	15	-
	inner	~6	13	46	40	-
Coating 'C' using low carbon ferrochrome and rotating retort	outer	~3	?	66	22	?
	middle	~8	14	68	18	-
	inner	~9	13	50	37	-

Table I: COMPOSITION OF THREE CHROMISED COATINGS AS OBTAINED BY E.P.M.A.

Condition of powder	Percentage Chemical Composition$^+$				
	Chromium		Iron		Chloride(Cl^-)
	sol in HCl	sol in H_2O	sol in HCl	sol in H_2O	sol in H_2O
Before regeneration i.e. after use	33.9-41.9	0.45-0.79	14.3-18.0	0.03-0.05	0.59 0.95
After regeneration	38.6-47.9	0.30-0.58	16.9-20.0	0.02-0.05	0.50-* 0.88

*Before NH_4Cl is added

$^+$Balance is Al_2O_3 and Cr_2O_3

Note: even after use, there are sufficient active ingredients to chromise effectively without regeneration but, with time, oxide coating of ferrochrome reduces activity. All powders after regeneration produced coatings within the required specification of 13-17μm.

TABLE II: COMPOSITION RANGE OF POWDERS IN USE BOTH BEFORE AND AFTER REGENERATION (TAKEN FROM ROUTINE ANALYSIS RESULTS)

Test Piece Identity		Outer Layer	Inner Layer	Growth Layer
156 2/6	L	+ P	+	+
216 3/6	L	+ P	+	+
232 4/4	L	+	+	+
214 6/6	L	+ P	+	(+)
226 6/6	L	+	+	(+)
A	L	(+)	+	(+)
B	H	MONO-LAYER		
274 6/6	H	MONO-LAYER		
275 1/4	H	MONO-LAYER		
008 4/6	H	MONO-LAYER		
258 3/5	H	MONO-LAYER		
269 3/6	H	MONO-LAYER		

Key

L = low carbon ferrochrome
H = high carbon ferrochrome
\+ = readily visible
(+) = just visible
P = some pores visible
A = flat test piece dynamic process
B = flat test piece static process

TABLE III: RESULTS OF FRACTOGRAPHS MADE PRIOR TO X-RAY DIFFRACTION ANALYSIS

Zone	% by weight	Sample Identity						
		A	B	C	D	E	F	G
Outer	*Cr*	53.6	70.7	70.2	67.0	68.7	71.8	0.2
	Fe	25.0	5.7	6.0	6.1	6.3	3.4	81.6
	C	12.6	10.7	12.2	11.5	11.7	11.7	11.3
	O	3.7	4.0	4.3	4.0	4.0	4.1	2.1
	N	4.7	8.4	6.8	9.0	9.0	8.4	2.8
Middle	*Cr*			58.7	69.6	68.8	60.6	
	Fe			21.0	6.1	6.7	17.4	
	C			11.7	11.4	11.9	12.5	
	O			3.8	4.0	4.1	4.3	
	N			4.4	8.4	8.3	4.6	
Inner	*Cr*	48.4	53.0	42.8	52.0	54.3	41.9	
	Fe	30.0	26.5	34.2	26.2	22.8	37.8	
	C	13.3	12.2	12.6	13.4	13.6	12.7	
	O	3.5	3.7	5.6	3.7	4.1	3.5	
	N	4.3	4.1	3.9	4.2	4.5	3.7	

Note: the 'zone' is the same as used elsewhere in this work in relation to the three-layer coating.
Samples A-F were all of the new coating.
Sample G was of the base steel of the pin in Sample B and shows how unreliable are all the values
For *C*, *N*, and *O*. What may be said is that there may be some *N* in the outer layer.

TABLE IV: EXAMPLES OF ANALYSIS RESULTS OF COATINGS OBTAINED BY E.P.M.A.

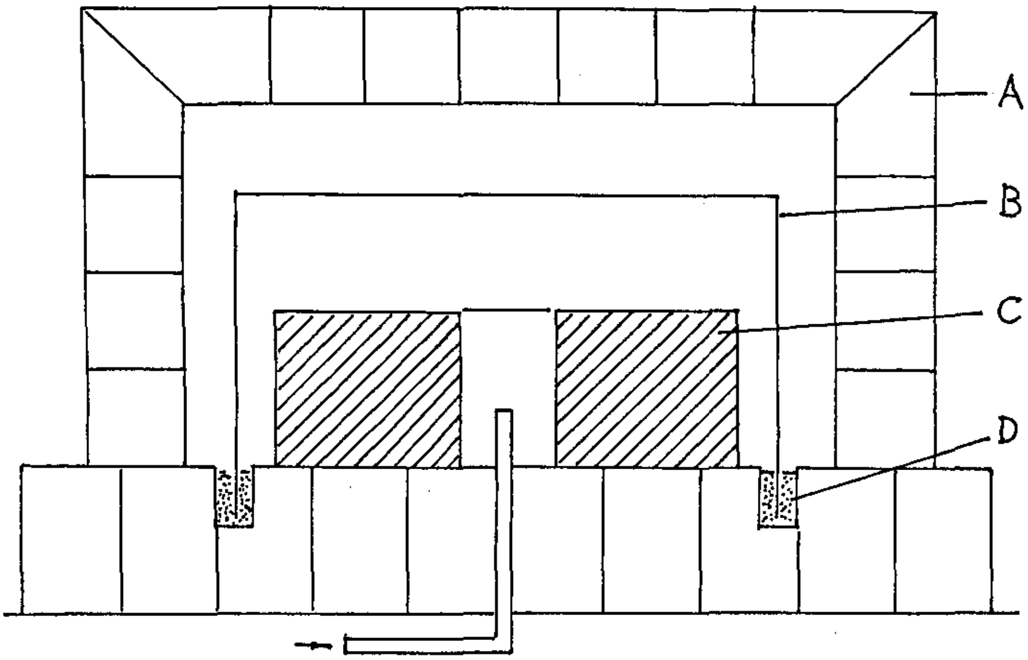


Fig. 1 Typical bell-type furnace as used in B.D.S. chromising process. The central pipe is for the introduction of the various gases as required, exit being via the sand seal. Furnaces seen were gas fired.

Key

A.	Gas-fired bell-type furnace
B.	Inner bell
C.	Charge in doughnut retort. This can be in individual boxes.
D.	Sand seal

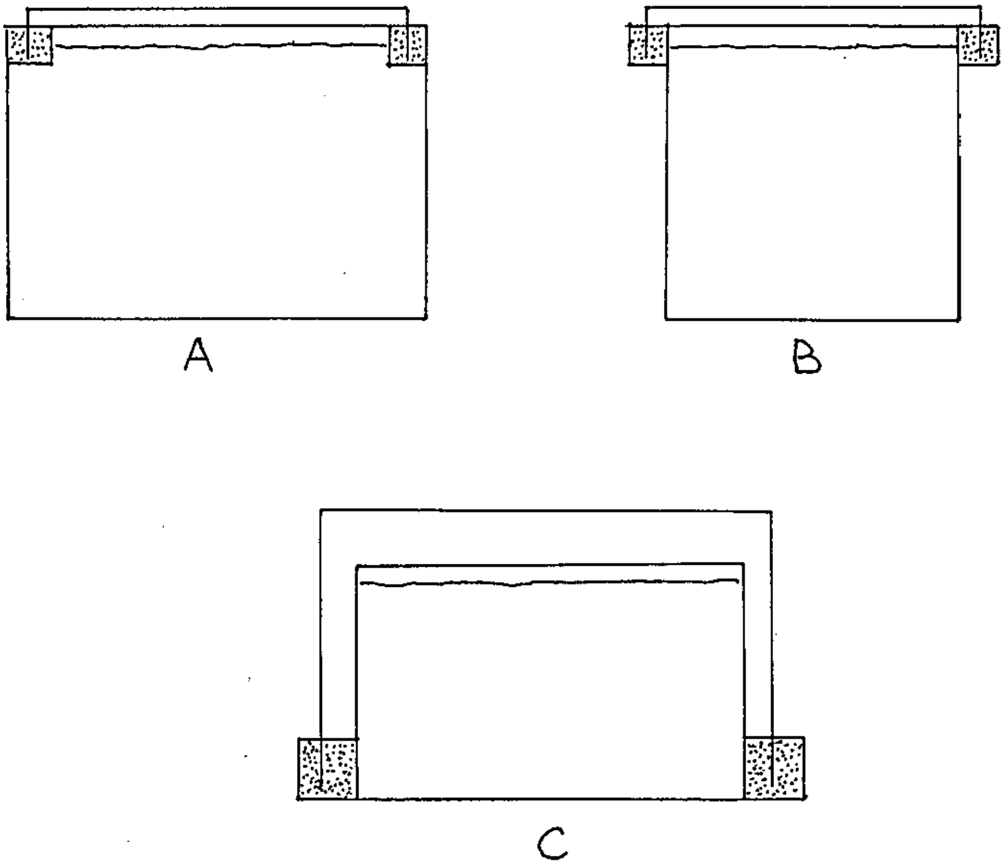


Fig. 2 **Retorts used in D.A.L. chromising process, and showing position of powder line together with fusible seal channels.**

Key

A. Box with internal seal
B. Box with external seal
C. Cover and tray system

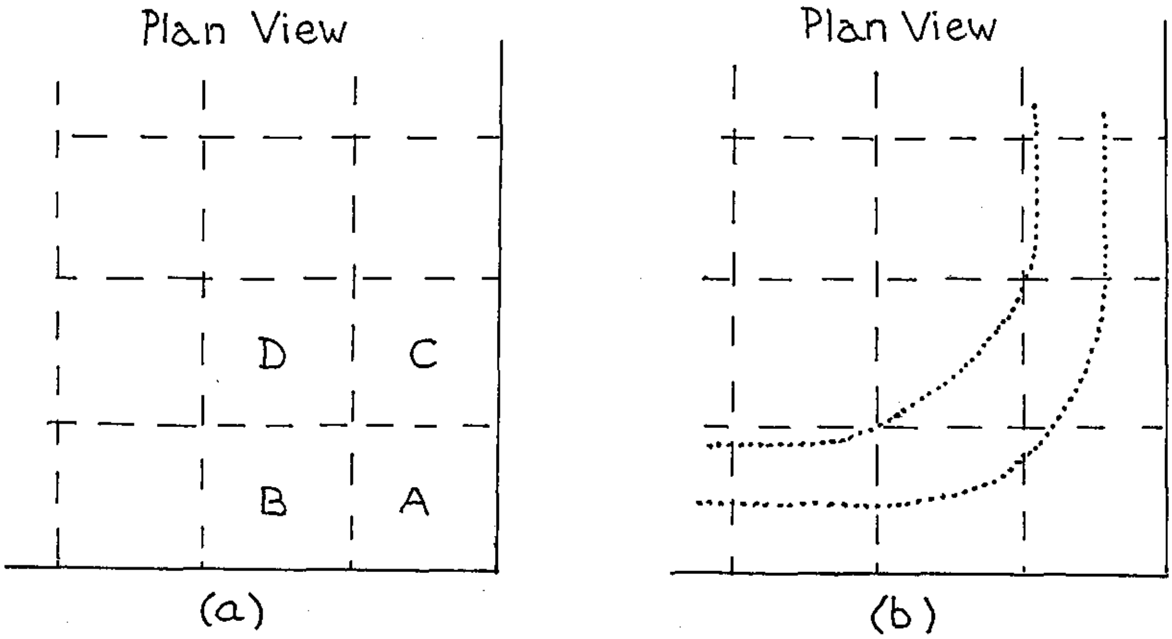


Fig. 3 **(a) Heat input with rectangular retorts**

(b) Isothermals developed during process

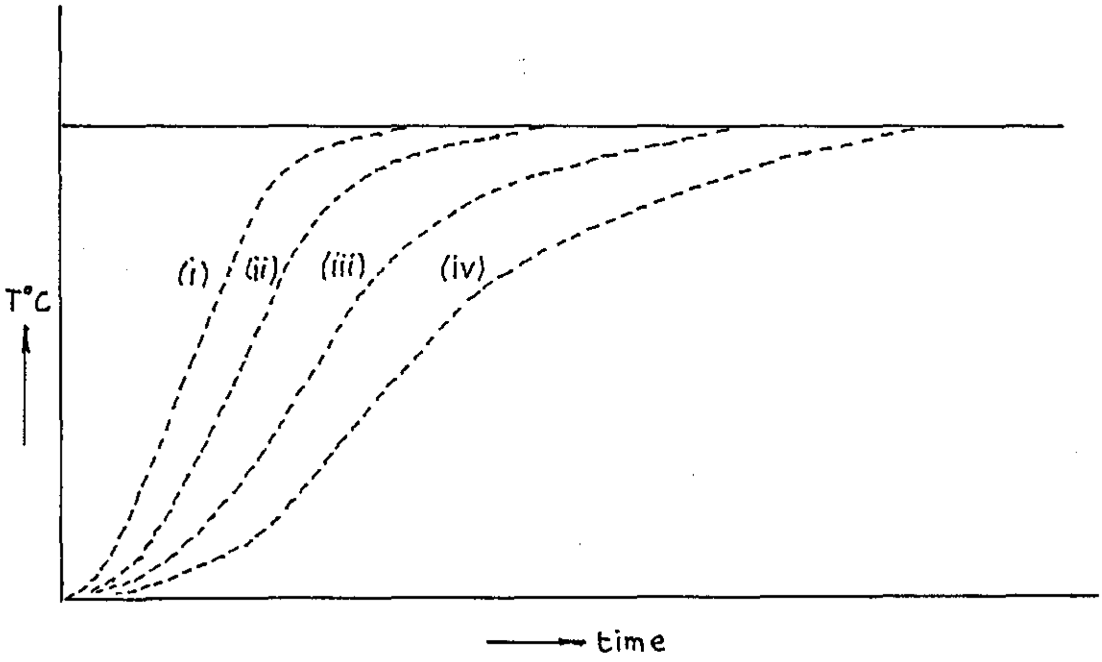


Fig. 4 **Time/temperature cycles in different parts of retorts (schematic).**

Key

i. Furnace controller
ii. Box corner
iii. Middle to centre
iv. Centre

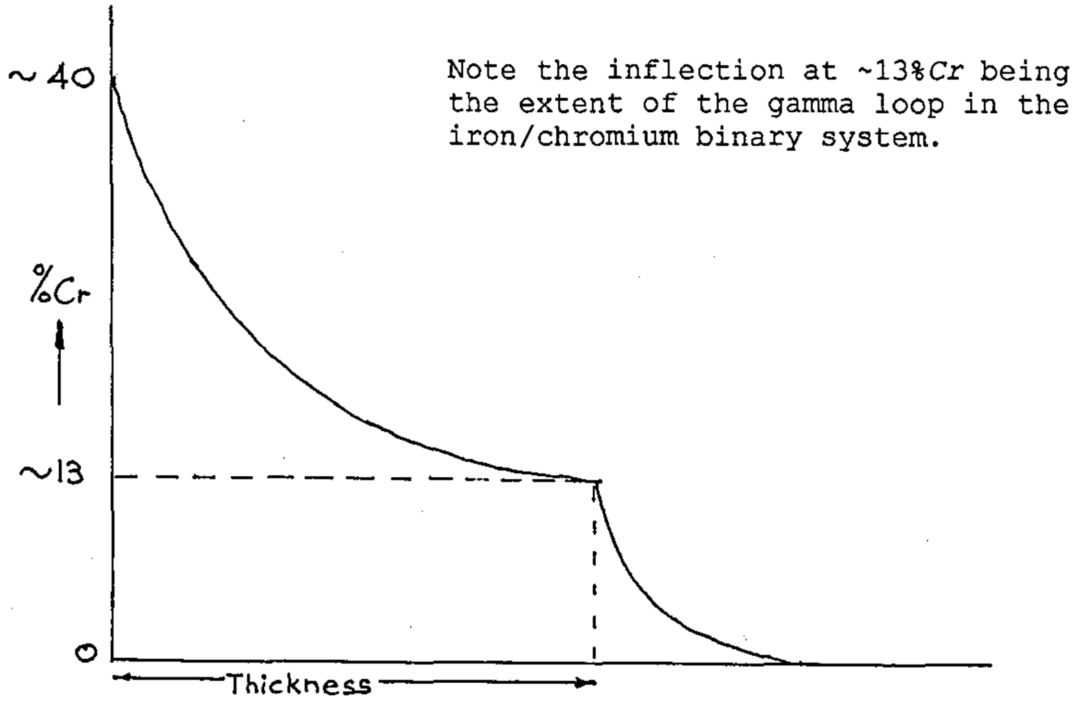


Fig. 5 **Typical composition gradient for chromium as found with low carbon steels. The area under the curve will be predominantly a solid solution.**

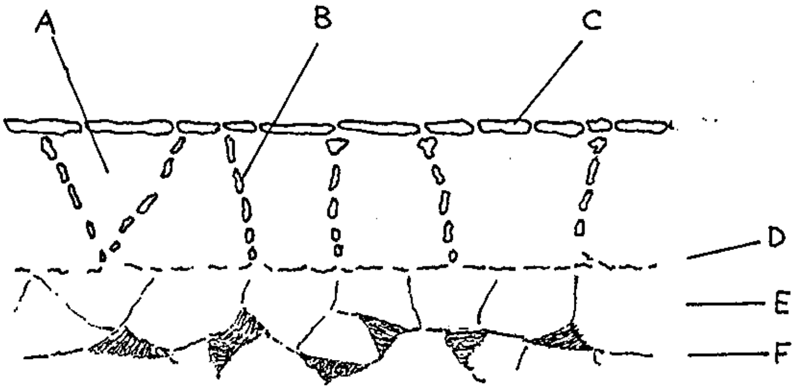


Fig. 6 **Section through chromised coating on 0.2% carbon steel. This is very sectional dependant. Nital etch.**

Key

A.	Chromium enriched ferrite
B.	Carbides at grain boundaries
C.	Thin carbide outer layer
D.	Extent of 13% *Cr* and gamma loop
E.	Zone of decarburisation
F.	Ferrite and pearlite of substrate

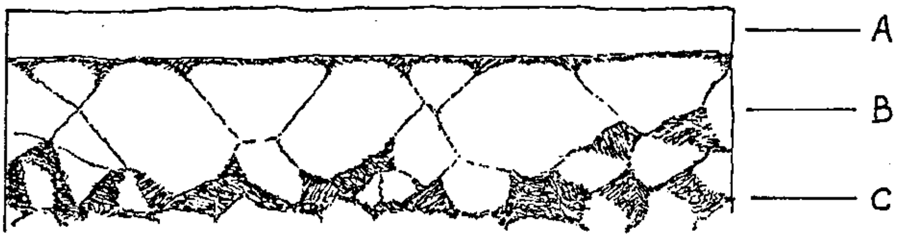


Fig. 7 **Section through chromised coating on 0.3 - 0.5% carbon steel.**

Key

A. M_xC_y carbide
B. Zone of decarburisation
C. Ferrite and pearlite of substrate

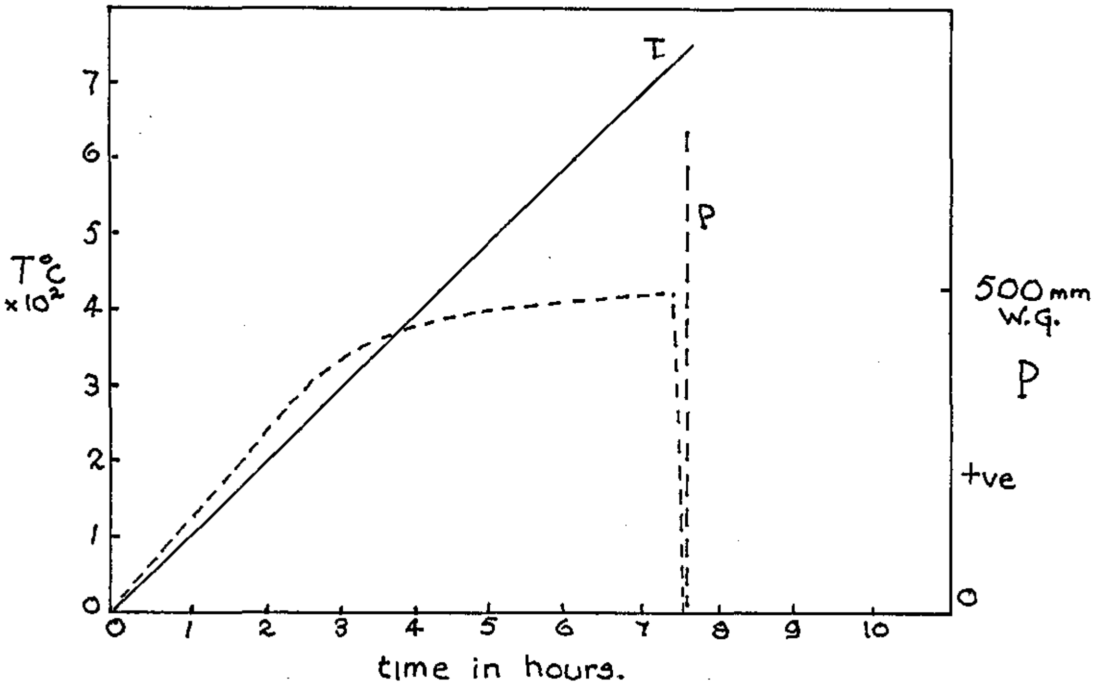


Fig. 8 **Retort pressure/time in small chromising retort heated at constant rate from ambient. Note explosion after pressure became negative and drew in air.**

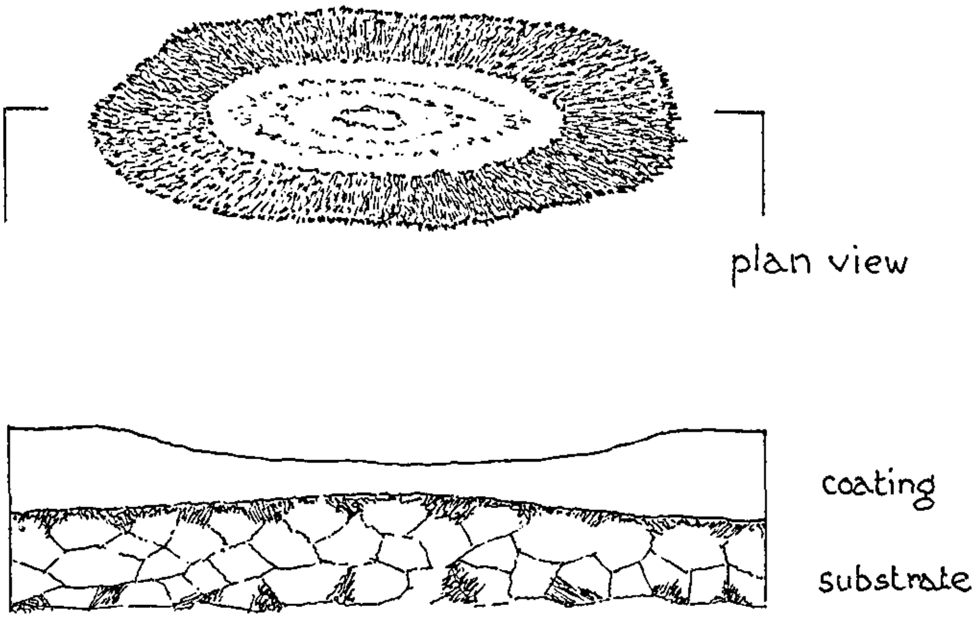


Fig. 9 Effect on coating of two parts in physical contact during chromising. The centre sections may even weld together. Actual shape will vary.

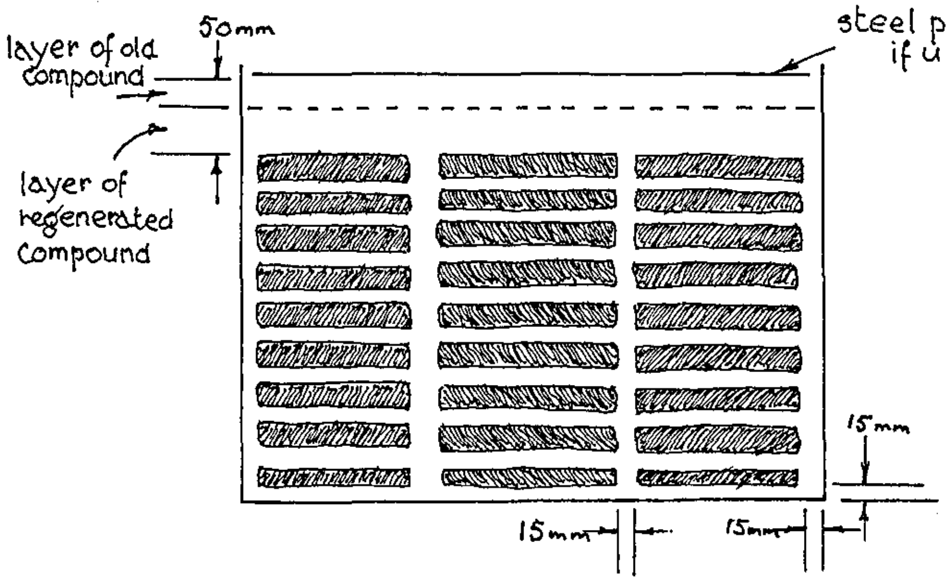


Fig. 10 The conventional method of packing a retort for chromising particularly with the D.A.L. process.

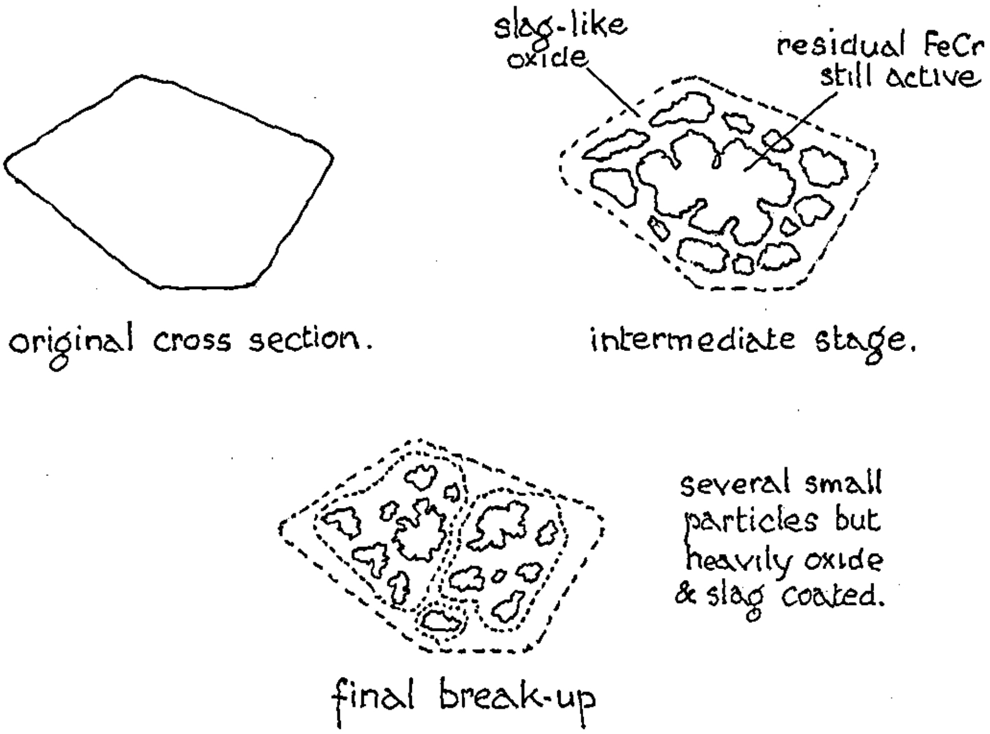


Fig. 11 Degradation of ferrochrome particles with use in D.A.L. process

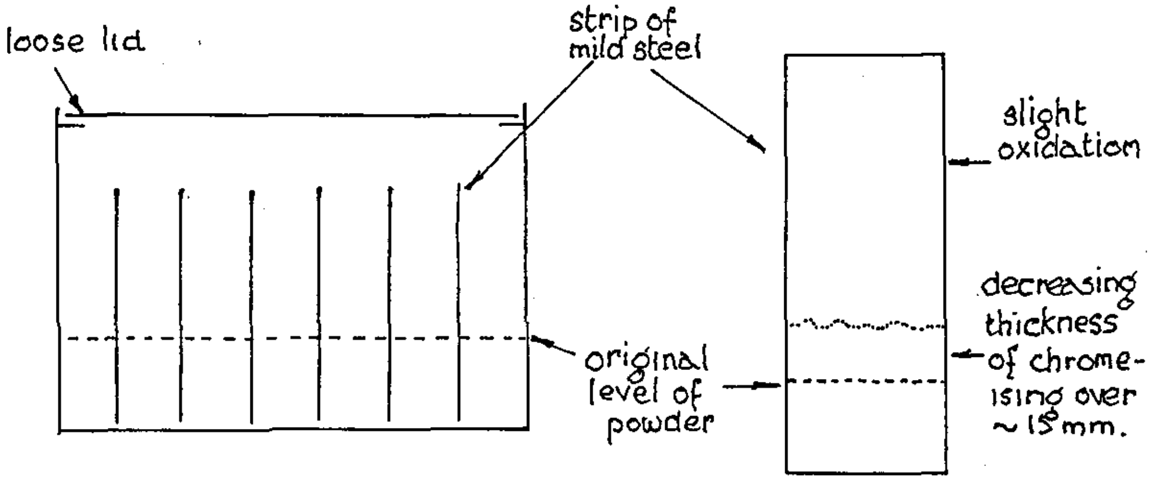
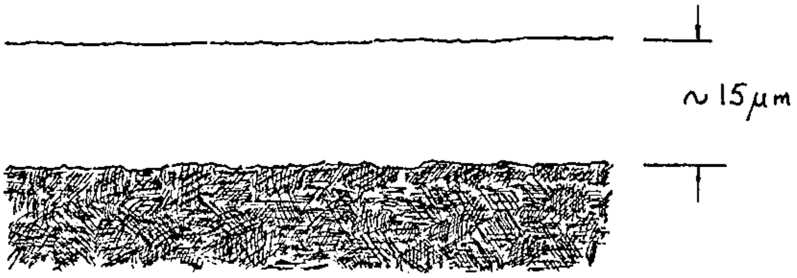
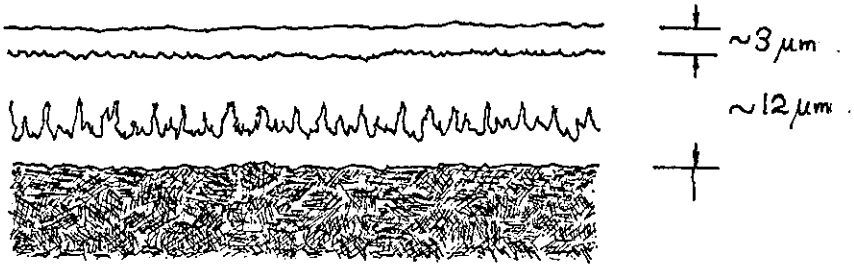


Fig. 12 Illustration of how 'throwing power' of pack chromising may be assessed.

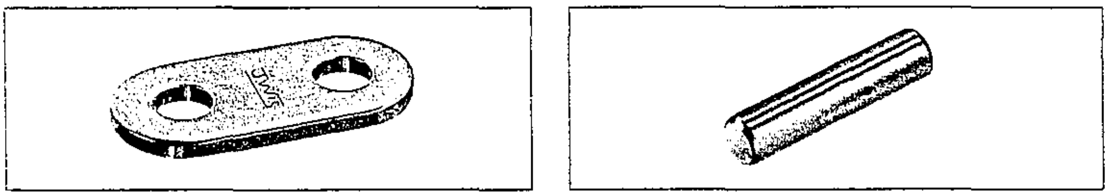


(a) Previous type of coating consisting of a straightforward single layer of carbide overlying a quenched and tempered martensite.



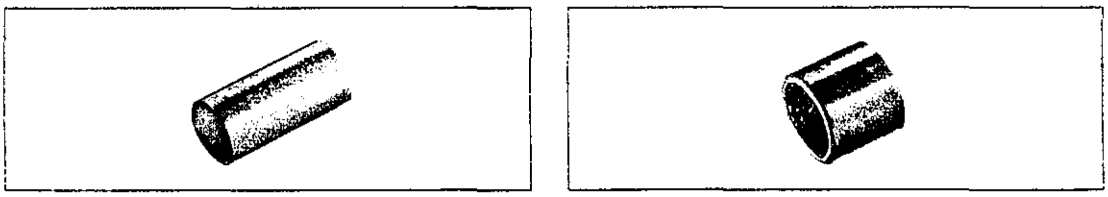
(b) Superior performance chain pin coating consisting of outer layer of carbide but with some nitrogen, overlying an inner layer of carbide which itself appears to consist of two different phases or constituents. Note columnar demarcation.

Fig. 13 Structure (schematic) of chromised coatings found on (a) standard and (b) superior chain pins. Both etched in Murakami's reagent.



Lasche/*Plate/Eclisse/Pieza de unión*

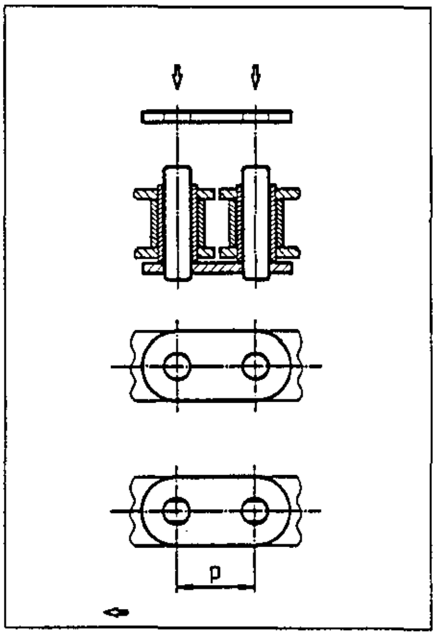
Bolzen/*Pin/Boulon/Pasador*



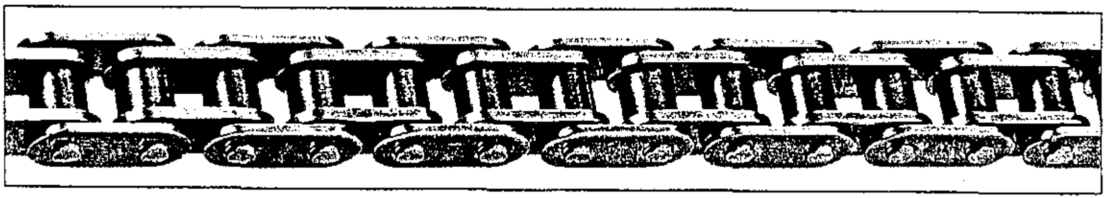
Hülse/*Bush/Douille/Casquillo*

Rolle/*Roll/Rouleau/Rodillo*

(a)



(b)



Kette/*Chain/Chaine/Cadena*

(c)

Fig. 14 Diagram of chain components.

(a) the separate items
(b) showing assembly; 'p' is pitch
(c) an assembled length

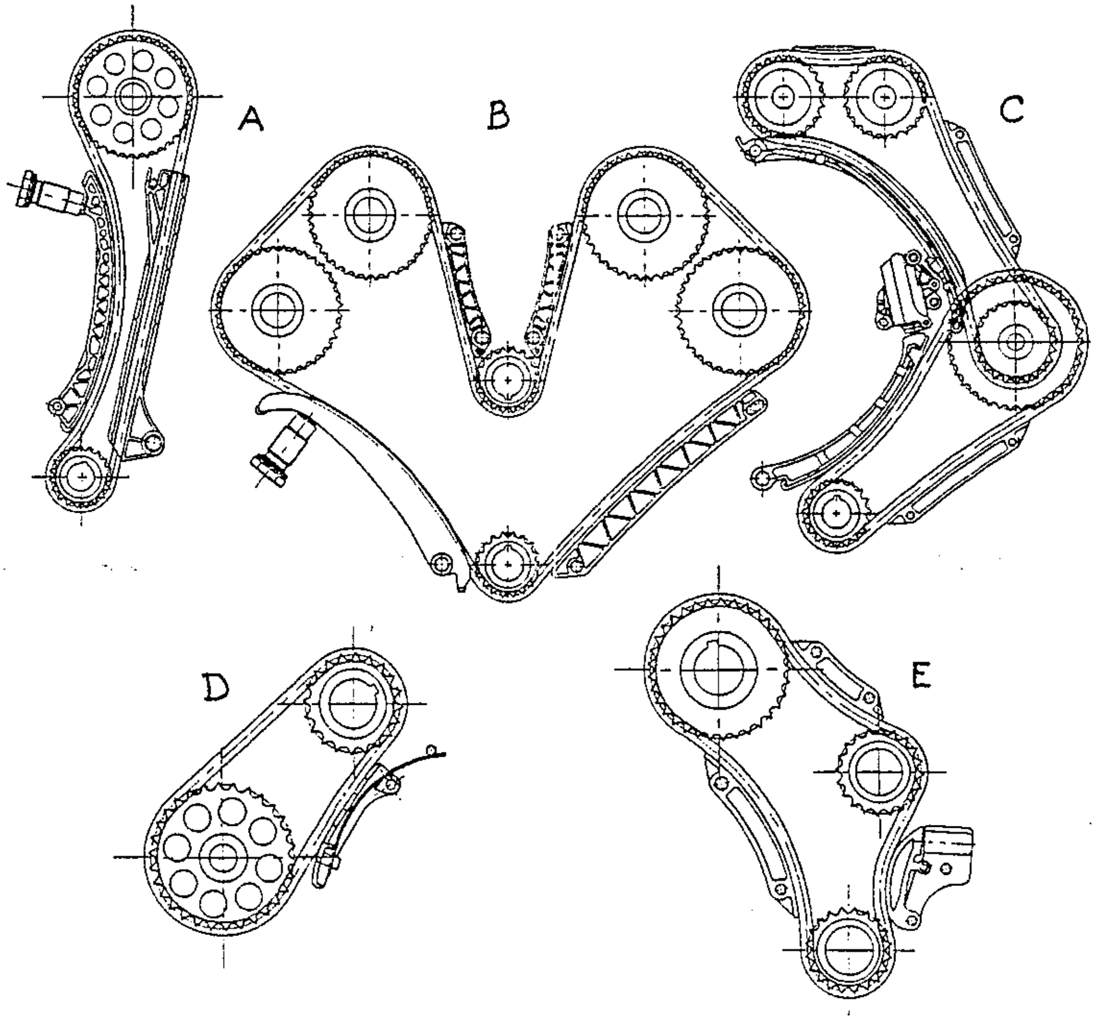
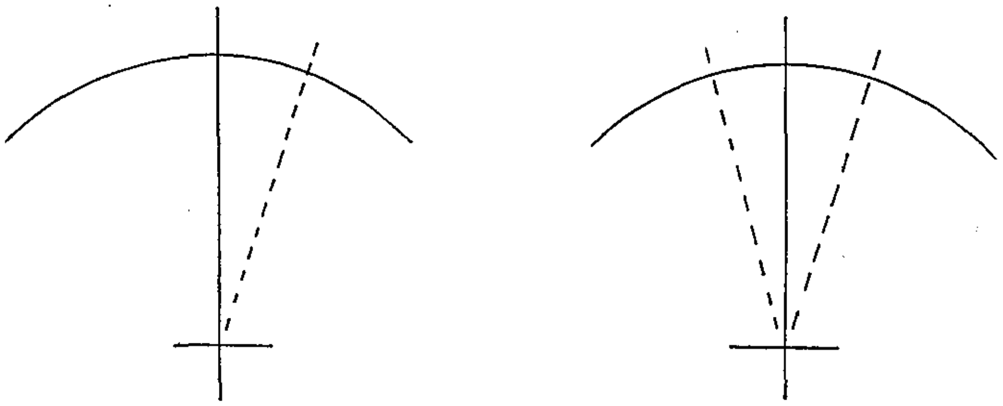


Fig. 15 Typical arrangements of chains in engines.

Key

- A. 3 Cylinder single O.H.C.
- B. V-8 Cylinder double O.H.C.
- C. 4 Cylinder Diesel direct injection
- D. Oil pump drive
- E. Oil pump and counter balance drive

Note: Tensioners and guide channels.



(a) normal around sprockets

(b) as around twin cam and auxiliary drive to oil pump and dynamo

Fig. 16 **Typical arcs of movement of adjacent links. See also Fig. 15**

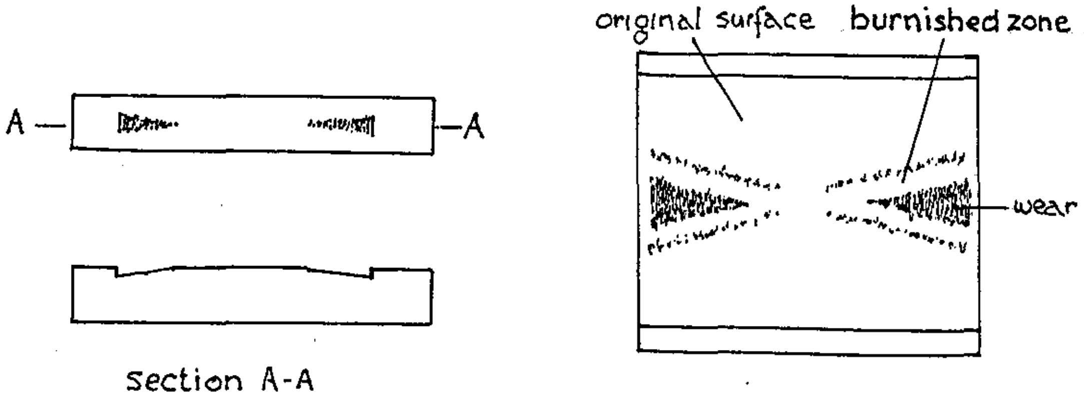


Fig. 17 **Typical wear pattern on a chain pin and bush. Scale exaggerated.**

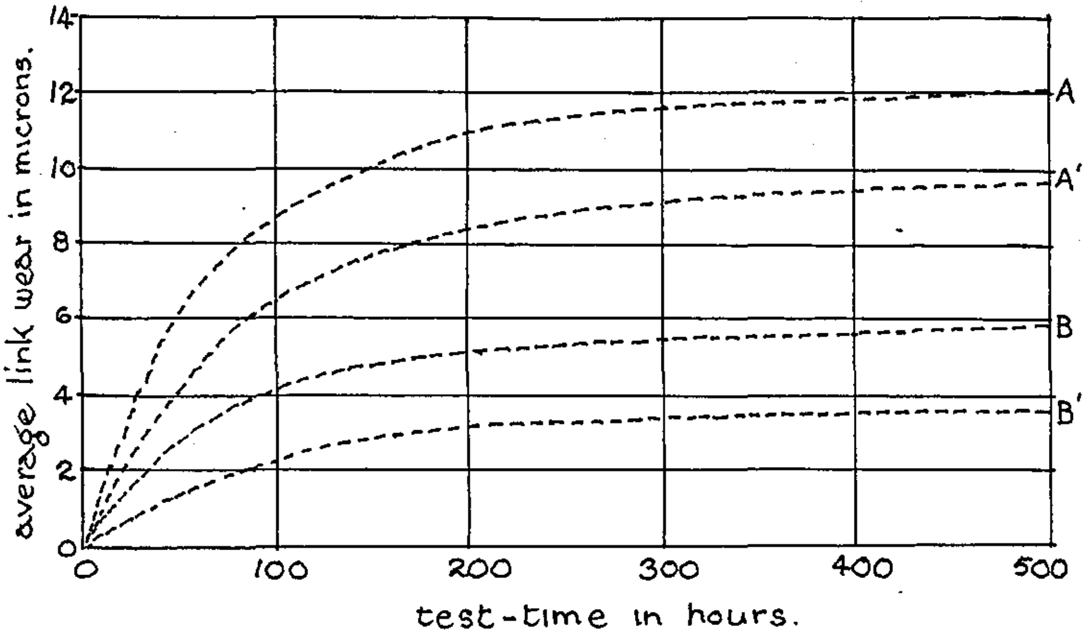


Fig. 18 **Typical time/extension curves obtained from chain test-rigs showing effect of old and new chromising practice.**

Key

A-A^1	Chain made with pins chromised by old process
B-B^1	Same chain as for A-A^1 but pins chromised by new process.

Note: the average link wear embraces wear on both pin and bush and any extension in total length for other reasons e.g. creep, loosening at riveted end of pin etc. but these are usually small by comparison with normal wear.

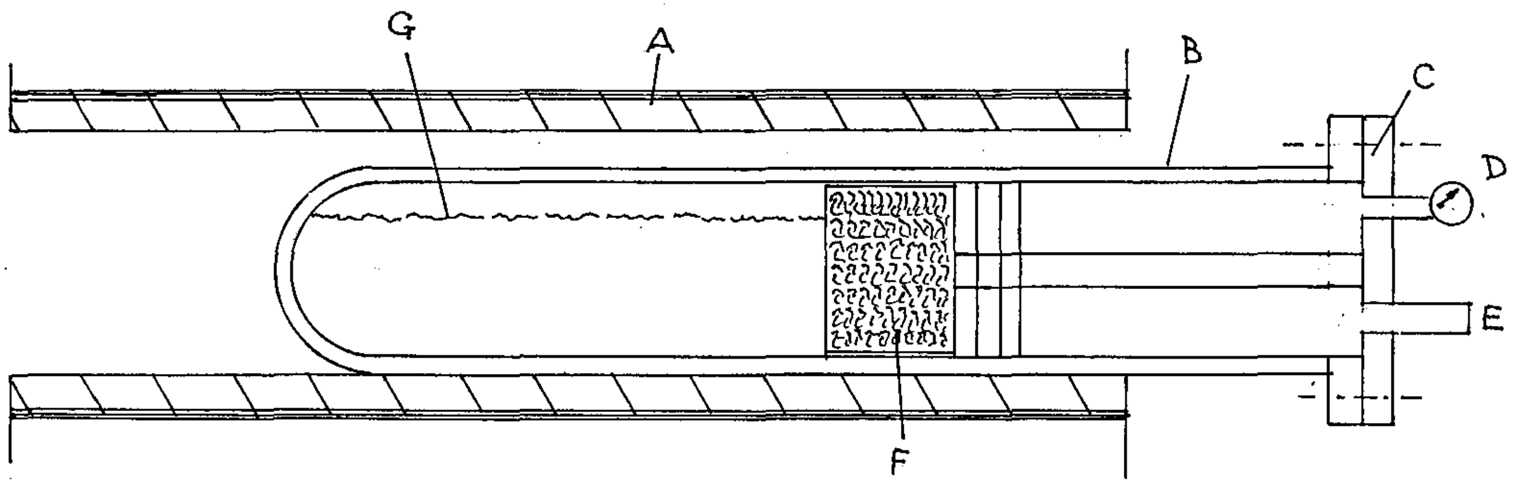


Fig. 19 **Typical barrel chromising retort and position in furnace.**

Key

A. Rotating furnace tube
B. Retort lying in furnace tube
C. Bolted on cover plate
D. Pressure gauge
E. Pressure control and relief valve
F. Insulating capsule and heat shields
G. Approximate top of charge when at rest

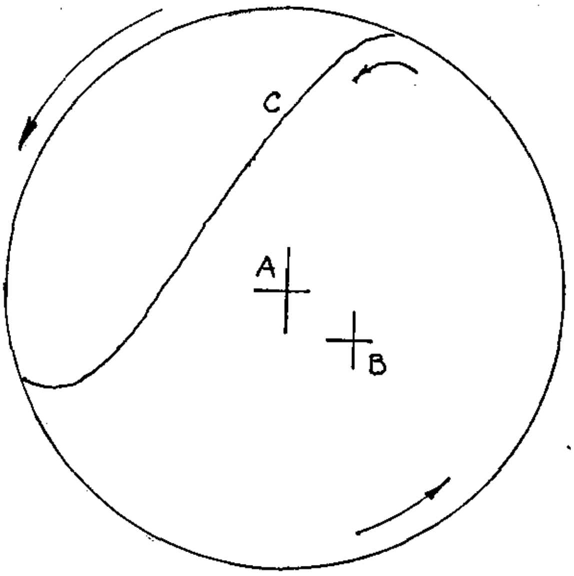
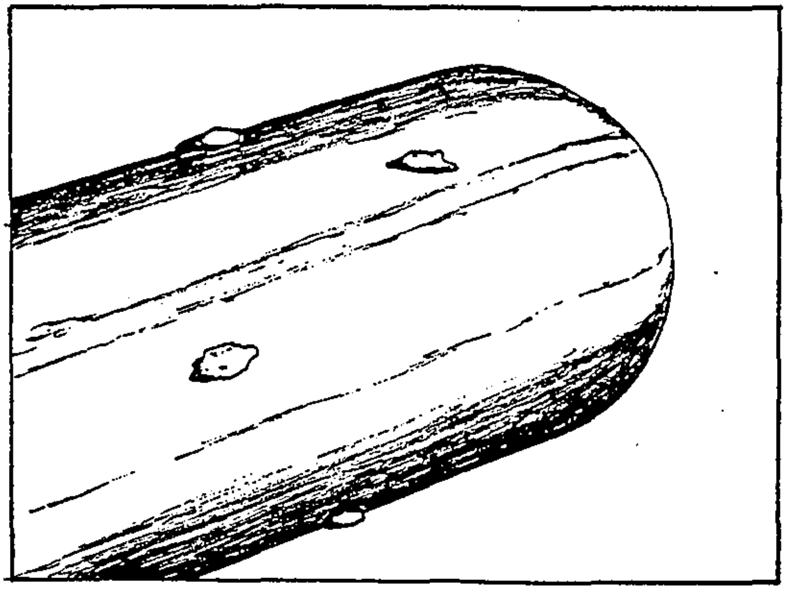


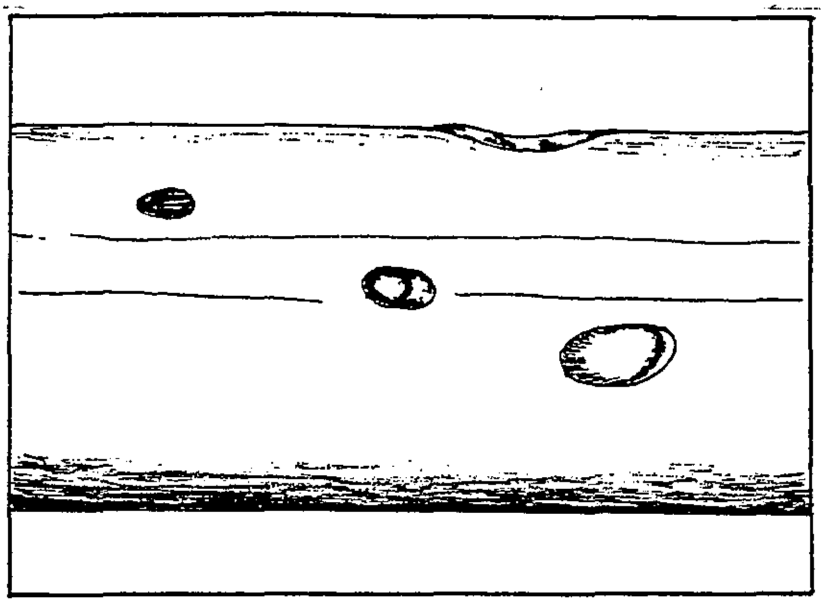
Fig. 20 Movement of charge during rotation of retort.

Key

A. Centre of retort
B. Rotational centre of charge.
This is a potential dead zone for movement.
C. Cascade face

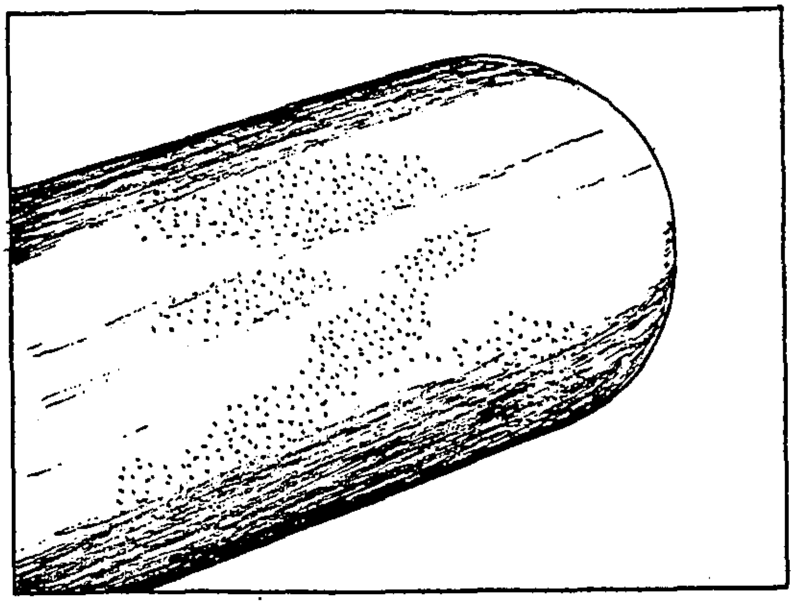


(a) Small particles of ferrochrome sintered onto surface. Often but not always associated with slag.

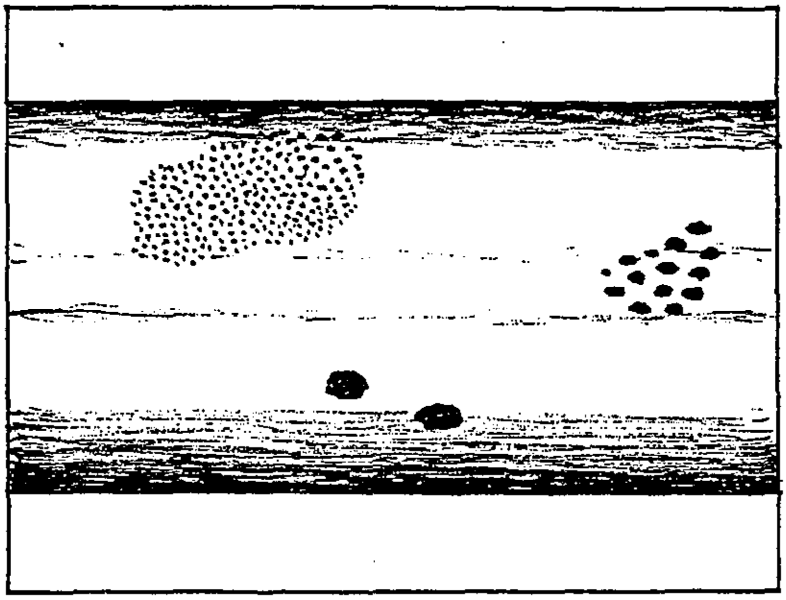


(b) Small slag defects showing holes, some full of slag, others empty. Note how surface is fluxed away.

Fig. 21 **Some of the surface defects found in earlier process.**



(a) Roughness caused by general corrosion before chromising.



(b) Three types of corrosion pitting occurring after chromising. All are filled with debris.

Fig. 22 Corrosion defects found in chromised pins.

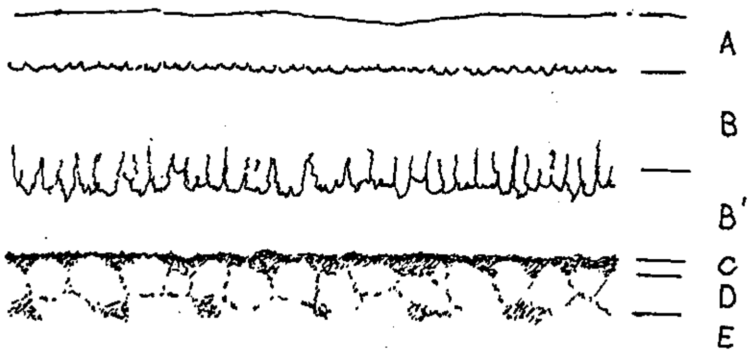


Fig. 23 Section (diagrammatic) through coating on chain pin, chromised with low carbon ferrochrome illustrating how term three-layer coating arose.

Key

A. Outer layer ~3µm
B. and B^1 two inner layers
C. Slight increase in pearlite
D. Decrease in pearlite (from carbon loss to coating)
E. Base steel, ferrite and pearlite

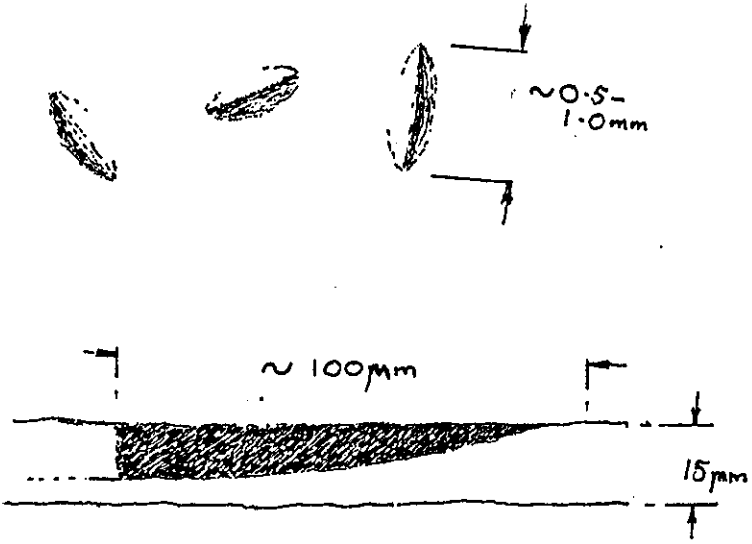


Fig. 24 Illustration of 'fish-scale' defect which can occur in box process.

Cross section showing how semi-elliptical piece of coating fractures and 'jumps' out.

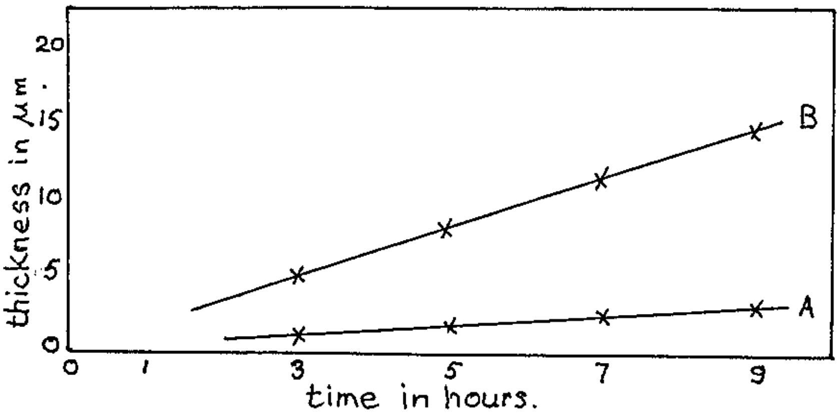


Fig. 25 Rate of growth of outer layer A and total coating B with time at furnace temperature of 1000°C.

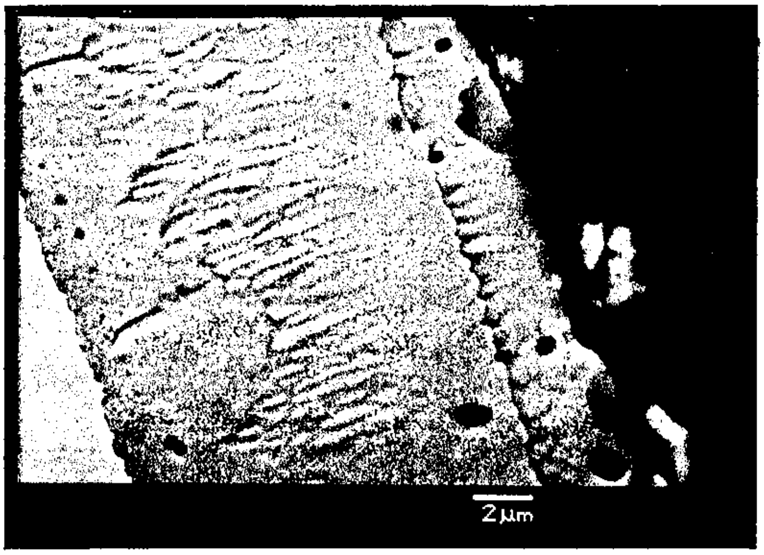


Fig. 26 Electron micrograph of typical three-layer coating.

Fig. 27 Section through occluded alumina defect.

Note: particles are predominantly within the range 1-5μm.

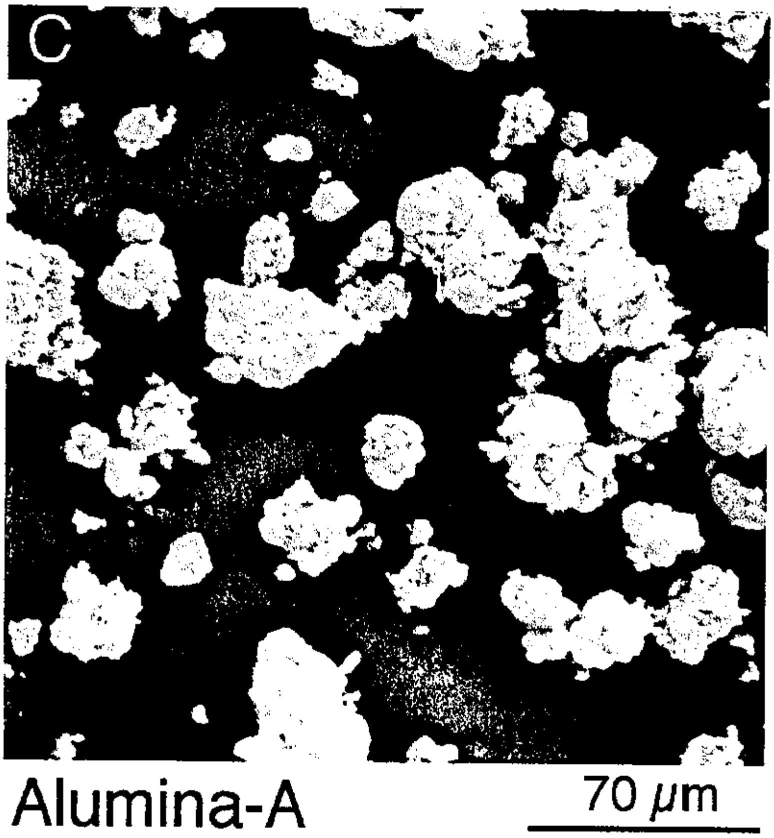


Fig. 28 Structure of calcined alumina.

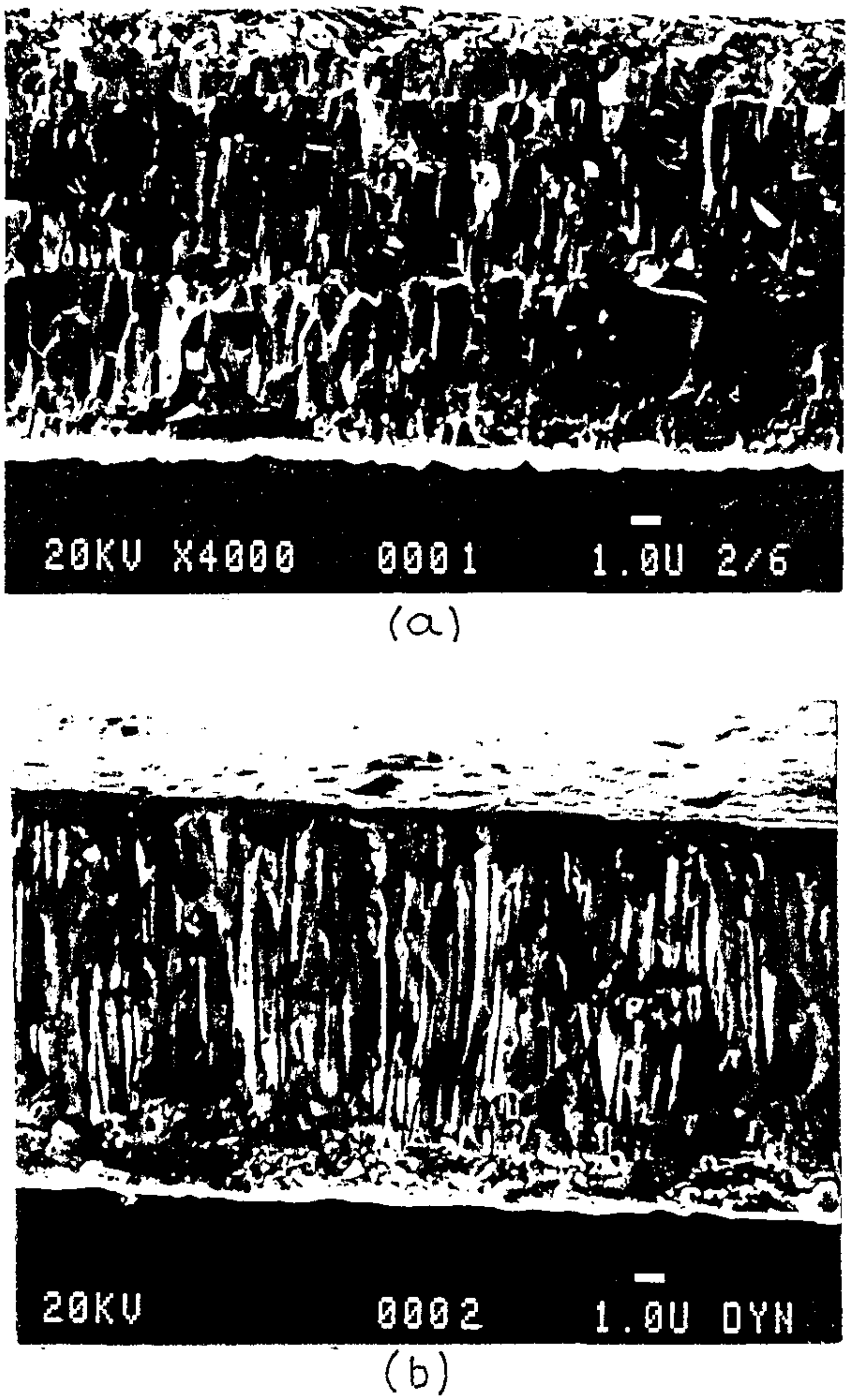
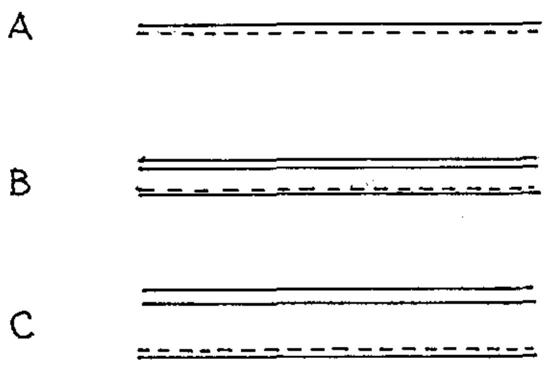


Fig. 29 **Electron micrographs of fracture faces of hard chromised coatings, see Table III.**

(a) Test piece 156 2/6 showing triple layer.
(b) Test piece B showing mono-layer



broken line is original surface.

A. This is very early state at < 1µm thick when a chromium rich layer forms at the lower temperature before diffusion speeds up. This could contain nitrogen.

B. With higher temperatures diffusion of all constituents increases to form carbides but outer layer persists and thickens more slowly. Some slight penetration of substrate by chromium.

C. Final coating of carbide overlaid by carbo-nitride.

Fig. 30 Growth sequence of new coating.

REFERENCES

1. A.R. CASTLE and D.R. GABE International Materials Reviews 1999, Vol 44, No.2. 37-58.

2. 'METALS HANDBOOK' 8th edition, Vol. 1, 13: 1961, Metals Park, OH, ASM.

3. E. SULLY: 'Metallurgy of the rarer metals – 1 Chromium'. 1st edition; 1954, London, Butterworth Science (2nd edition, (with E. A. Brandes), 1967).

4. R.L. SAMUEL and N.A. LOCKINGTON: Met. Treatment., 1951, 18, 354, 407, 444, 495; 1952, 19, 27, 81.

5. G. BECKER, K. DAEVES and F. STEINBERG, Stahl u. Eisen, 1941, 64, 289, 294.

6. L. LAISSUS. Rev. Metall. 1926, 23, 155.

7. U.K. PATENT 516,260

8. B.I.O.S. Report on 'Chromising of Steel Surfaces' C.XXXIX-14 1946.

9. D.E. LEHANE and R. WACHTELL, Prod. Eng. 1956, 27, 180.

10. Iron Age, 1957, 180, 128.

11. CHROMALLOY CORPORATION. Bulletin 502, 'Chromising Solves Pump Problem'.

12. Chem. Eng. 1961, 68, 188.

13. E.H. MAYER and R.M. WILLISON, Ind Heat. April and May 1969, 36, 685-692, 885-894.

14. N.S. GORBUNOV, Diffuse Coatings on Iron & Steel, The Ac. Sc. of the U.S.S.R. Moscow 1958 (in Russian).

15. A.N. MINKEVICH. Chemicothermal treatment of metals and alloys, 1965 Moscow, Machinostroeneinie (in Russian).

16. C.F. POWELL, J.H. OXLEY, J.M. BLOCHER (Eds). Vapor Depositon, 1966, ELEC. CHEM. SOC. NEW YORK, J. WILEY.

17. T. ARAI, J. Heat Treatment, 1979, 1.1 (2), 15-22.

18. F-S CHEN *et al:* Materials Chemistry and Physics 1998, 53, 19-27, Elsevier.

19. T.P. HOAR and E.A.G. CROOM, J. Iron & Steel Inst. 1951, 169, 101.

20. R.L. SAMUEL, MUREX REVIEW, 1958, 1, 501-527.

21. C.C. HANSON, UNPUBLISHED WORK 1961-1987.

22. H. DORNER, N.A. LOCKINGTON & A. KEMPSTER: UNPUBLISHED WORK 1950-1987.

23. Y. KOMEN *et al*: Journal. Iron & Steel Inst. May 1968, 206, 487-493.

24. J. TACIKOWSKI & W. LILIENTAL: Proc 16th Int. Heat Treatment Conf, 1976, 31-39, Met. Soc, London.

25. P. GALMICHE: Compt. Rend., 1950, 230, 89-91, 1181-1183; Rev. Metall., 1950, 47, 192-200; Met. Finish., 1951, 49, (1) 61-64.

26. N.V. KARYAKINA & G.N. DUBININ: Phys. Met. Metallography, 1960, 9, 832.

27. C.C. HANSON: Examination and Report on the Chromising Process at J. WINKLHOFER & SÖHNE, Aug 1990 (1&2). Second Addendum, Dec 1990 (3). Private Circulation.

28. F.P. BOWDEN and D. TABOR: 'The Friction and Lubrication of Solids', 1st edn; 1950, O.U.P. (1958 edn. issued in Classics Series 2001).

29. 'METALS HANDBOOK', 1948 Edition. A.S.M. Metals Park. Ohio.