

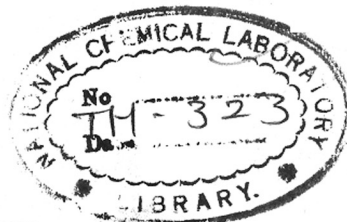
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COMPUTERISED

AN ELECTRON DIFFRACTION EXAMINATION
OF THE BRASS SURFACES EMPLOYED FOR RUBBER TO
METAL ADHESION.

By

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INTRODUCTION. ^{COMPUTERISED}

The twentieth century has seen a great increase in the application of machinery, and incorporated in each unit, whether rolling-mill or aircraft-engine, there have been rotating or reciprocating mechanisms; and associated with these mechanisms there have come the subsidiaries - vibration and noise.

At first, the designer, satisfied in fulfilling the intended purpose of the machine, inclined to neglect these latter, which he considered as being natural consequences. However, it was gradually realised that the prevention of vibration could improve the performance of a machine and lengthen its working life to a very great degree. Even if it were not possible to overcome inherent vibration, a great advantage lay in preventing its transmission to other parts of the structure, because disastrous had been the results when the natural frequency of the source coincided with the resonant frequency of the structure. Noise, a specialised instance of vibration, received at first even less attention; it was accepted and seems even to have been glorified as the prerogative of the machine. Practical research in industrial psychology has shown that excessive noise will always result in nervous fatigue to those who have to endure it, although

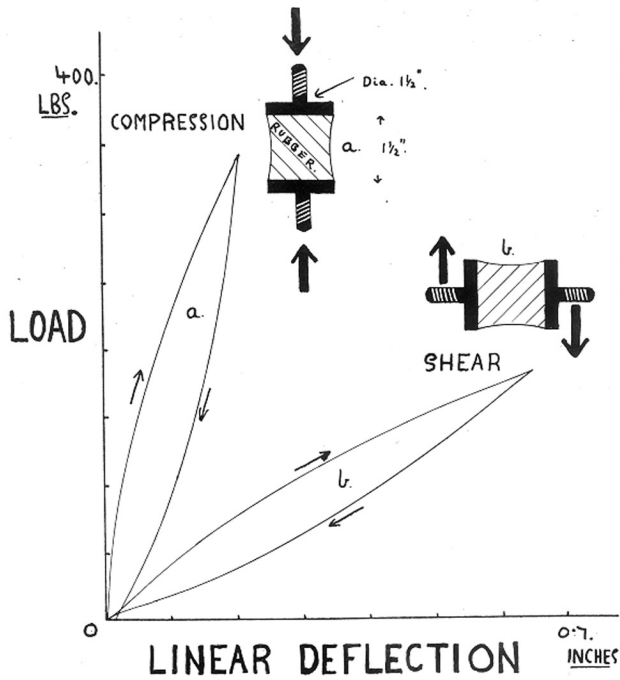


Figure 1. Diagram illustrating increased deflection for a given load when rubber is employed in 'shear' as compared with compression.

a soft rhythmical noise may have a beneficial effect.

In order to overcome vibration, there is required a material or system which will

- a. Prevent the transmission.
- b. Absorb the energy.

A steel spring can only satisfy the first requirement but some external damping system (i.e. shock-absorbers) becomes necessary to absorb the energy. However, the peculiar physical properties of rubber can make it very effective for both the above purposes. The resilience and hysteresis of rubber can be varied within wide limits by control of the vulcanisation and the composition of the rubber stock. It is these two properties which are employed respectively for prevention of transmission, and absorption of, vibration. The early applications of rubber employed blocks of material secured in some form of compression, but in order that rubber shall function as a spring it is essential that there be free space for distortion. This freedom is available only at the edges when considering a block in compression, and a large load is required for any deformation. However Fig.1 shows how much more advantageous it is to use rubber in shear rather than in compression (the term "shear" referring mainly to the relative motion of the two metal faces, since the force in the rubber is a complex resultant of shear and tension). Rubber in tension

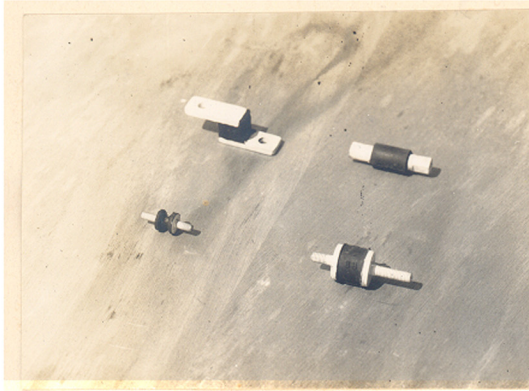


Figure 2.

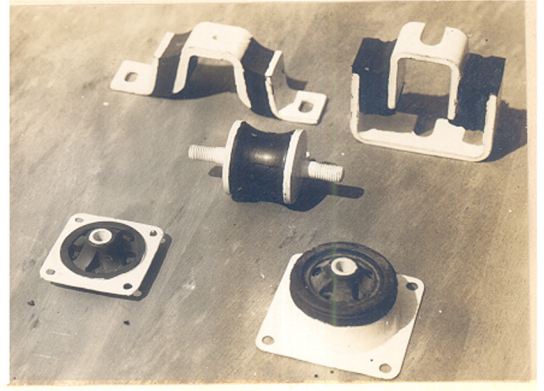


Figure 3.

Various Anti-vibration Units.

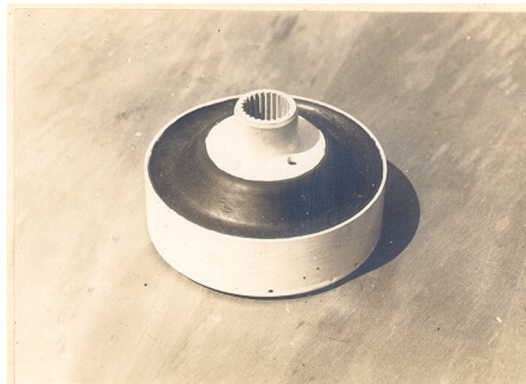


Figure 4. Universal Shaft Coupling.

alone could equally well be employed, but is not favoured because the design of mountings becomes complicated by the need for a superstructure and also the provision of safety stops is less feasible. Rubber in shear therefore makes it possible to construct a very efficient anti-vibration system, but only if there is available some method by means of which the rubber may be caused to adhere to the metal pieces with a strength at least equal to the ultimate tensile strength of the rubber. As is described later, this is feasible and around the production of this rubber/metal bond there has rapidly arisen a large industry. Various mountings are illustrated in Figs 2 and 3 and besides their use as anti-vibration mountings, rubber-bonded units have been developed for shaft couplings and universal joints (e.g. Fig.4 capable of withstanding a torque of 9,000 ~~w~~.lbs.). Marine propeller shaft couplings are manufactured to transmit a full 3,000 H.P. In particular are these couplings useful in allowing motors to direct-drive pumps and other machinery. A considerable degree of both parallel and angular misalignment can be ignored when such units are employed.

It is not unusual in a technical process, for which there is a great industrial demand, that practice far outstrips theory, and well has this been exemplified by the industry in question. During the war the production of bonded units

has increased extensively and more severe have become the conditions which they have been required to withstand. Unfortunately when failures or difficulties arose, these were often impossible to understand and to correct because too little was known about the theory of the process which had developed in an empirical fashion. Research was therefore undertaken by the author to investigate some of the fundamentals of the process, the intention being thereby to explain the problems interfering with urgent production.

For a fundamental study, information was required about the chemical composition and physical nature of the surfaces involved, both before and after bonding. Diffraction methods were the most useful means of investigation. X-rays cannot successfully be used for the determination of true surface structure since the penetration is at least 10^5 A. and in the case of thin electrodeposits (with which this research is particularly concerned) the diffractions caused by the surface layers are swamped by those from the underlying material. On the other hand, in the grazing incidence method of electron diffraction, the penetration will not be greater than 30 A. The bonding of metal to rubber is throughout a series of surface processes and electron diffraction methods, making use of the Finch camera, were adopted as being ideal for fundamental studies on the above process.

CONTENTS.

	Page
CHAPTER I.	
THE RUBBER/METAL BONDING PROCESS	6
 CHAPTER II.	
AN ELECTRON DIFFRACTION EXAMINATION OF THE BRASS PLATING PROCESS	24
 CHAPTER III.	
AN ELECTRON DIFFRACTION EXAMINATION OF THE BONDING PROCESS	53
 SUMMARY AND ACKNOWLEDGMENTS	63
 REFERENCES.	

C H A P T E R O N E .

T H E R U B B E R / M E T A L B O N D I N G
P R O C E S S .

The methods available for the bonding of rubber to metals may be classified as follows:-

- (a) Mechanical keying.
- (b) Cements and adhesives.
- (c) Metallic interlayers.

MECHANICAL KEYING.

This consists of vulcanising rubber into dovetailed and undercut grooves on the metal surface, but is now obsolete. However, grooving is sometimes practised in conjunction with methods (b) and (c) in order to increase the available surface area.

CEMENTS AND ADHESIVES.

There is available a multitude of proprietary cements and adhesives which, with widely varying effectiveness, will secure rubber to metal. The method is popular because of its simplicity but in general the bond strength is not high and the joint is thermoplastic. A particular application is for securing a rubber lining in metal tanks and pipes.

METALLIC INTERLAYERS.

When rubber is vulcanised in contact with certain metals it has been found that very strong adhesion can be obtained without any employment of an intermediate cement or adhesive. The design of the greater proportion of rubber/metal components requires that the metal portions be fabricated in steel or in some cases cast iron - strength and cheapness being the reasons. However rubber vulcanised in contact with either of these materials secures no adhesion. Consequently various processes have been evolved, by trial and error methods, making use of an interlayer of another metal which adheres strongly to rubber after vulcanisation; this interlayer may be applied by chemical displacement, electrodeposition, hot dipping, or spraying.

The earliest reference to this technique of bonding is a patent by Adams [1] in 1897. Iron or steel objects were first coated with copper and rubber was then vulcanised in contact with them. Other metals appear to have been used empirically in the following years, but much was hidden in trade secrets. In 1904 Weber [2] showed that those metals which most readily formed stable sulphides gave good adhesion to rubber, stating that antimony was the best. Following this, there appeared patents and articles [3,4,5,6,7,8] from 1904 - 1914 covering the use of various binary and ternary alloys, at least one component of which readily formed a

sulphide. Thereafter, up to the present times, the patent literature quotes a host of metals and alloys as being suitable for adhesion. Time and practice have shown that there was much wishful thinking and it must be assumed that many of the results were purely fortuitous.

Poor adhesion, the need for a critical rubber stock, special processing conditions, and lack of reproducibility have overwhelmingly eclipsed these methods in favour of a simple interlayer of alpha brass (approx. 70% copper and 30% zinc). Although tried earlier, this method was developed industrially in the U.S.A. between 1920 and 1930 and is in great use today; its popularity lies in three reasons.

- (i) Great strength of bond (1,000 lbs./sq.in.)
- (ii) Avoidance of a thermoplastic bond.
- (iii) Latitude in choice of rubber stocks.

Hot-dipping [9] and spraying [10] have been employed to provide the brass layer upon the ferrous object but both methods are liable to leave oxidised surfaces which are detrimental to bonding. The electrodeposition of brass has therefore proved the most popular and successful. Because of the large number of variables which control the ultimate chemical composition, the electrodeposition of brass on an industrial scale was long regarded as a difficult art. However, modern methods of control analysis have simplified the process very considerably.

BRASS PLATING.

In the cases of copper and zinc the normal deposition potentials are wide apart. But for any metal M in a solution of the corresponding ions $M^{n\oplus}$, the single potential e is given by the equation

$$e = e_0 + \frac{RT}{nF} \log_e \left\{ M^{n\oplus} \right\}$$

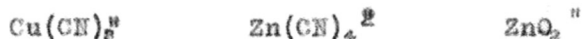
where e = standard metal potential of the given metal and metal ions, $\left\{ M^{n\oplus} \right\}$ = activity of $M^{n\oplus}$, which approximately equals $\left[M^{n\oplus} \right]$ the molar concentration of $M^{n\oplus}$ in g. mols per litre.

From a solution of its ions, a metal can only be deposited when the single cathode potential is more negative than e . From the above equation it is seen that e is a function (but logarithmic) of the activity, or approximately the concentration, of the metal ions. Therefore the deposition potentials of copper and zinc can be made to approach one another by adjusting the concentration of the respective ions. In a sulphate solution this would require an impossibly low concentration of copper ions. However, the addition of sodium cyanide will bring about the formation of complex cyanides. The cuprocyanide ion is the most stable of these complexes and the cuprous ion concentration is reduced to such an extent that the reversible potential approaches that of zinc. The simultaneous deposition of

zinc and copper at the cathode now becomes possible, the deposit being a true alloy, brass, and not a mechanical mixture.

The complex ions present in a brass plating solution are probably the following:-

Major Complex Ions.



Minor Complex Ions.



The relative concentration of these ions and their dissociation to metal ions is controlled by physical and chemical conditions of the solution. The major change is the increase in zincate ion concentration as the pH is raised.

Since the relative rates of deposition of copper and zinc from the complex cyanide solution depend on the respective deposition potentials, which in turn are influenced by the degree and nature of ionisation present, variation in chemical and physical conditions will control the ultimate composition of the deposit.

Such variables are:-

Total metal concentration (Copper and Zinc)

Copper /Zinc ratio in solution

Uncombined cyanide concentration*

* Being defined as sodium cyanide present in excess of that amount calculated to form the compounds $\text{Na}_2\text{Cu}(\text{CN})_2$ and $\text{Na}_2\text{Zn}(\text{CN})_4$.

pH.

Current density.

Temperature.

Agitation of the electrolyte (which aids diffusion).

It is the general practice to aim at depositing a layer of brass containing 70% Cu and 30% Zn. Whilst it has been claimed [1] that the composition of the brass for rubber adhesion is critical it seems generally agreed [12, 13] that brass with a copper content of 60-75% gives an equally good bond.

The effect of most of the above variables on the composition of the deposit has been described by Coats [14] and more recently by Clarke, Bradshaw and Longhurst [18]; and the following is a summary.

The copper content of the brass is raised by:-

1. Increase of temperature.
2. Increase of current density.

The copper content is lowered by:-

1. Increase of ammonia content.
2. Increase of pH.
3. Increase of Zn/Cu ratio in bath.

These relationships are not linear.

The efficiency of deposition (cathode efficiency) is raised by:

1. Increase of temperature.
2. Increase of ammonia.

3. Increase of pH (slightly).
4. High total metal content.
5. Agitation of the electrolyte.

The efficiency of deposition is lowered by:-

1. Increase of current density.
2. Increase of uncombined cyanide.

Many brass plating baths have been devised and employed with slightly differing combinations of the above variables. (See, for example, Coats [14], Pan [15], Hogaboom [16] and Young [17]). The compositions are usually within the following limits:-

Copper and zinc content (total)	- 20-35 g.p.l.
Copper/Zinc ratio	- 3 : 2.
Uncombined cyanide	- 5-15 g.p.l.
Current density	- 3-10 amps/sq.ft.
Temperature	- 20-40°C.
pH	- 9.5 - 12.5

It is the custom to fix all these factors except pH and temperature, the adjustment of these giving a simple and effective day to day control of the composition of the plate.

Brass plating from solutions such as these has served well, but the rate of deposition is rather slow. Brass deposits for rubber adhesion are seldom required to be greater than a maximum thickness of .0001". Therefore the

time of deposition has not been considered as a urgent economic factor. However, certain industrial processes, other than rubber bonding, have required a thicker deposit of brass in a shorter time [18]. This could not be accomplished with the previously described type of solution since the necessary increase of current density caused the cathode efficiency to fall off and the copper content became too high. Following on certain results of Oplinger [19], a new type of brass plating bath has been recently developed [18, 20, 21]; current densities up to 40 amps/sq.ft. were employed to deposit 70/30 brass. The cathode efficiency was maintained by an increase in the total metal concentration and the zinc content was raised considerably to check the tendency towards high copper brass. A typical composition is Zinc - 30 g.p.l.; Copper - 15 g.p.l.; Na_2CO_3 - 20 g.p.l.; Uncombined cyanide - 4-8 g.p.l.; pH - 12.6-12.8; Temperature - 55-60°C.

This represents a break away from the older methods in which the copper/zinc ratio of the solution approximated to that of the deposit required. As far as is known at the time of writing this type of brass-plating bath has not been applied in the rubber bonding industry, but it shows promise. A disadvantage lies in the comparatively high operating temperature of this bath necessitating an efficient fume-exhaustion plant to save the operator's health.

THE PROCESS OF BRASS PLATING.

SELECTION OF BASIS MATERIAL.

As mentioned previously iron and steel are the metals most frequently to be brass-plated, and they should be free from slag inclusions, porosity and other defects; Jevons has described [44] imperfections which are to be avoided. Many other metals, such as the light alloys [22], can be brass-plated, though stainless and case-hardened steel are exceptions - to these there is an extremely poor adhesion of the brass because ^{of} the intermediate oxide, carbide, or nitride layers. Deeply recessed components are undesirable because, although the throwing power of a brass bath is relatively high, the composition of the brass in these recesses may not be 70/30.

PREPARATION OF BASIS METAL.

Cold-rolled mild steel or cast-iron objects are often coated with heavy scale. The removal of this is effected by sand-blasting or scratch-buffing. Following this, the components are mounted on well spaced jigs and pass through the cleaning cycle, of which the following is typical:

In sequence

- a. Trichlorethylene degreasing.
- b. Cold water swill.
- c. Alkaline cleaner ("Zonax").
- d. Hot water swill.
- e. Acid pickle; 15% H_2SO_4 (possibly assisted electrolytically).
- f. Cold water swill.
- g. Cyanide electrolytic bath 70 g.p.l. NaCN(optional).

The acid pickle is an effective method of removing scale. The action is chiefly mechanical, the acid penetrating between the scale and the metal; the liberation of hydrogen removes physically the scale from the underlying metal. Cathodic treatment assists to remove this scale by hydrogen evolution. Heavy pickling of cast-iron may leave a graphite film on the surface, which is to be avoided.

Silman [23] has described how certain wetting agents can advantageously be employed to improve the efficiency of the various cleaning stages.

Thorough cleaning and washing of the basis metal is essential and any omission in this process reflects in poor adhesion and patchy deposition of the brass.

PLATING PROCEDURE.

A rubber-lined steel tank is the most satisfactory and heating coils, etc. must similarly be protected. Iron or steel exposed to the electrolyte is to be avoided, the detrimental action of iron salts being discussed later in this thesis. Anodes are of 70/30 rolled cartridge brass; cast brass tends to form a passive film more easily [18].

The cleaned components, mounted in jigs, are hung on the cathode bus-bars and are plated for a period of 5 - 20 minutes. Agitation of the electrolyte is advisable to raise electrode efficiencies.

Some workers have recommended an intermediate metal coat upon the object before brass-plating; for example, copper by a strike plate [24] or zinc by hot-dipping [25]. However, if pre-cleaning is thorough, the direct adhesion of brass to steel is entirely satisfactory.

CONTROL OF THE PLATING BATH.

Daily analysis is essential. The composition of the electrolyte is controlled and any deficiencies are made up by the addition of the necessary salt. The composition of the deposit is checked at least twice daily by deposition on to test pieces of a similar type to those normally being plated.

Rapid methods of analysis have been described by Jernstedt [26]. Further methods have been given by Clark, Bradshaw and Longhurst [21]. Ammonia determinations still present some difficulty and improvements in the methods have been evolved by Monaweck [27] and Blow, Hiscox and Smith [28]. The polarograph appears a useful instrument for rapid copper and zinc determinations; all traces of cyanide must however be removed as it interferes with the current/voltage curves.

Carbonates slowly accumulate in solution and are not harmful in reasonable concentrations. A safe limit appears to be about 30 g.p.l. Na_2CO_3 , but opinions differ widely. If the concentration becomes excessive, carbonate may be removed by precipitation as described by Hull [29].

pH control can be effected colorimetrically using Alizarine yellow G.G. (pH 9.5 - 11.5) and Tropaeolin (pH 11.2 - 12.8). Electrometric methods are the most reliable and can be self-recording. A drawback lies in the large salt error of the normal glass electrode at high pH values, but an absolute pH value is not essential for control purposes. A special type glass, obtainable only in the U.S.A., has been described by Gray [30] which markedly reduces the salt error.

The pH is adjusted by adding sodium bicarbonate (to lower) or sodium hydroxide (to increase) to the electrolyte.

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Accurate control, both analytical and physical, coupled with a co-ordinated adjustment of variables enables a 70/30 deposit to be maintained from many months from one plating bath. The random or unrecorded adjustment of these variables leads only to chaotic results and here lies the explanation of the once-termed "mystery and art" of brass plating.

THICKNESS OF BRASS DEPOSIT.

The thickness of the brass deposit for rubber adhesion is not critical and usually lies between .00002" and .0002". Determination of the rate of deposition and thickness may be made by direct weighing of a test piece of known area. The thickness of an electrodeposit may also be determined by other means such as the magnetic gauge, microscope, drop tests, etc., available methods have been comprehensively described [43].

LENGTH OF SERVICE OF A BRASS PLATING SOLUTION.

During the life of a brass plating bath, the total metal content can be deposited at the cathode and renewed from the anode many times over. Nevertheless, the slow accumulation of carbonate, cyanate, iron salts, dirt, dust and organic matter limit the useful life. Continuous filtration is advisable and the average working life of a brass plating solution is in the neighbourhood of one year.

THE USE OF ADDITION AGENTS.

Such addition agents as arsenic, phenol, glue and gum were frequently added to brass-plating baths required for ornamental deposits. Their action is to brighten the deposit but the mechanism is obscure. The control of their concentration by analysis is extremely difficult, and their presence is not necessary in plating baths intended for rubber adhesion.

TREATMENT AND STORAGE OF BRASS PLATED SURFACES.

Satisfactory adhesion requires that rubber be vulcanised in contact with pure alpha brass; this necessitates that the surface be free from:-

- (1) Deposits due to lack of washing.
- (2) Its own corrosion products.

Requirement (1) is effected by washing in hot water followed by hot air drying. The wash water must be clean and not allowed to accumulate salts introduced by drag-in from the plating bath. Gurney [31] has stated that as little as $\frac{1}{2}$ mg. per sq.in. of sodium hydroxide or sodium carbonate, if allowed to dry out on the surface, will ruin adhesion. Buchan [32] describes the occlusion of electrolyte in porous metals, such as cast iron or Admiralty gun-metal, which causes staining of the brass.

Oils, stearates, etc., which are soluble in rubber may not be harmful.

An elaborate drying process is described by Ball, Murphy and the Dunlop Rubber Co.Ltd. [28] in which the brass plate is immersed in a series of solvents each miscible with its predecessor, e.g. water, alcohol, ethyl acetate and a solution of rubber in solvent naphtha.

Requirement (2) is the more difficult to maintain. It is not always convenient nor practicable to vulcanise rubber to the brass immediately after plating; the problem is therefore to retain an uncorroded brass surface until such time as the components are ready to be processed.

It has been stated that the brass plate must be used immediately [11, 34] or within 4-8 hours [36] but Merron [24] finds that a period of 48-72 hours is permissible. Many statements have been made that hot or humid atmospheres are to be avoided [35, 37, 24]. Air-conditioned rooms or airtight containers have been employed for storage and some plants close down when the relative humidity exceeds 64% [38]. The main point is that all those factors which will accelerate the corrosion of brass, such as moisture and heat, must be avoided.

The brass surface may be mechanically protected from corrosion by means of certain protective coats. The most

widespread method is to paint or spray the surface with rubber solution. Brass so protected may be stored for a much longer time (of the order of weeks), though a very humid atmosphere may still cause corrosion, the rubber film being always slightly porous. The composition of the rubber solution is not critical but it is recommended [38] that use be made of a benzol solution ^{of} stock somewhat harder than the final rubber. A compounded latex stock has been applied to the surface by electrophoresis [39].

Protective layers other than rubber include paraffin wax and cumarone resins, both of which are soluble in rubber during vulcanisation.

THE BONDING PROCESS.

Those areas of the brass plated component to which rubber adhesion is not required are "stopped-off" with a cellulose lacquer whilst rubber solution is painted on to the surfaces to be bonded. An unvulcanised rubber stock, compounded to have the required mechanical properties when vulcanised, is built to shape approximating to that needed in the finished article. This rubber and the metal parts are placed in position in a metal die which is then placed in a vulcanising press, the excess rubber being ejected. Vulcanisation and bonding takes place under conditions of

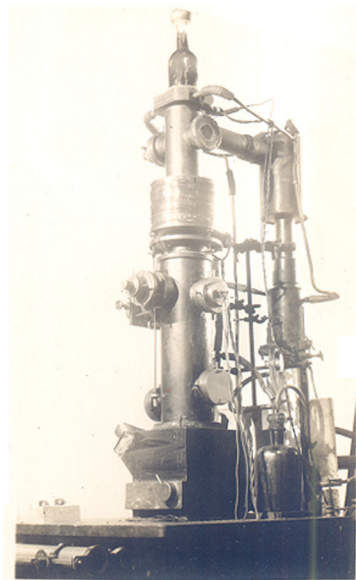
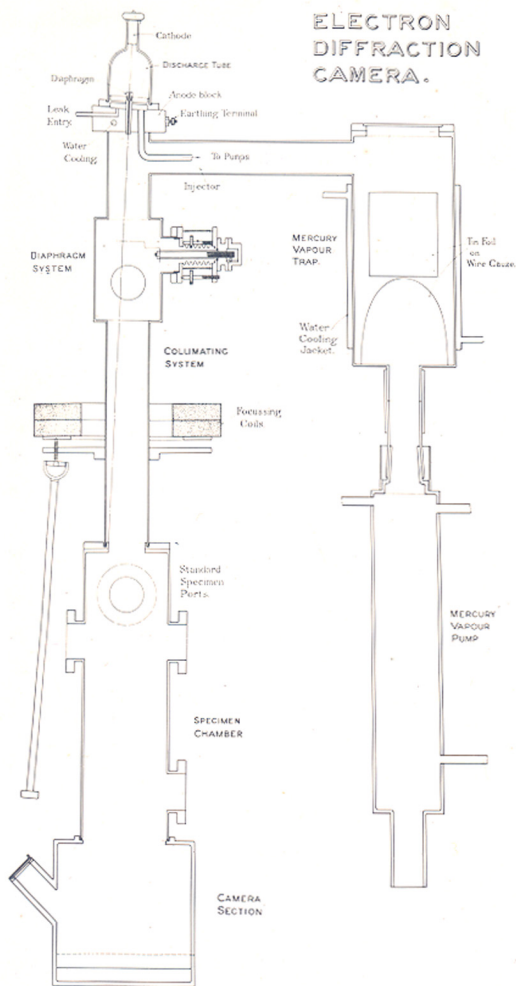
controlled temperature, pressure and time. On completion the components are removed, cleaned and submitted to various tests.

CHAPTER II.

AN ELECTRON DIFFRACTION EXAMINATION OF THE BRASS PLATING PROCESS.

Electron diffraction is now a fully recognised tool; the theory and technique have been comprehensively described elsewhere, particularly by Finch, Quarrell and Wilman [45] and Finch and Wilman [46]. In consequence only a brief description will be given here.

The Finch type camera illustrated in Figs 5 and 6 consists essentially of (1) a cold cathode discharge tube for generating a beam of electrons at a potential of about 50 Kv.; (2) a collimating section in which the beam is reduced in cross section by means of diaphragms and concentrated by means of the axial magnetic field of the focussing coil; (3) a diffraction section in which the controlled electron beam impinges on the surface of a specimen carrier; and (4) a camera section in which the diffracted electrons can be recorded visually on a fluorescent screen or recorded on a photographic plate. The whole camera is evacuated by a four-stage mercury vapour pump backed by a rotary pump. A constant voltage high-tension supply is necessary and this is obtained by



Figures 5 and 6. The Finch Electron Diffraction Camera.

employing a diode valve, run under saturation conditions, in the high tension line [47]. A limiting current of 1 milliamp. can pass to the cathode of the discharge chamber of the camera. A constant dynamic pressure is maintained in this discharge tube, thereby maintaining a constant potential between anode and cathode.

Much electron diffraction work has been done by transmission through films less than 10^{-6} cm. in thickness. This technique is not applicable to massive specimens, so in this case use is made of the "reflection" method, in which the electron beam skims down the surface of the material and the crystallites projecting from the surface behave as transmission specimens.

THE CATHODE DEPOSIT.

Preliminary electron diffraction examinations by Hillier [48] showed generally that the surfaces electroplated from current brass-plating electrolytes had the characteristic face-centred cubic structure of alpha brass. By control of the variables, described earlier, alpha + beta or beta brasses could be deposited and their electron diffraction patterns obtained.

Experimental.

These observations were confirmed (see Figs. 7, 8, 9, 10) but there was one anomaly: During a routine plating experiment several mild steel pieces of equal area were connected to the cathode bar and immersed in a standard Coats type brass plating solution. Fig. 11 illustrates these test pieces, measuring 1" x $\frac{1}{2}$ " x $\frac{1}{8}$ ", which could be subsequently bonded to rubber and tested for adhesion. From previous experience the current density was adjusted so that a 70/30 alpha brass deposit would be obtained (50ma/sq.in). It was noticed, however, that whereas some of the pieces rapidly received an electrodeposit of yellow 70/30 alpha brass, others took on the distinctive yellow-red of beta brass (55/45 approx.). Ten or fifteen minutes of plating was necessary to produce a gradual change to the normal alpha type. The existence of these respective phases of brass was checked by electron diffraction examination of the surface.

It was evident that certain of the steel pieces, presumably by virtue of a surface effect, were exerting a considerable influence on the nature of the deposit. It was noticed that, during the plating operation, that those surfaces receiving a high zinc deposit were characterised by a vigorous hydrogen evolution (gassing) from certain parts. A close inspection of these areas revealed the presence on the original surface of specks of oxide which had failed to be



Figure 7.
Electrodeposited
Alpha Brass.

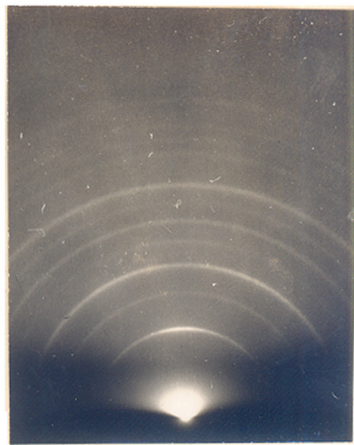


Figure 8.
Electrodeposited
Beta Brass.

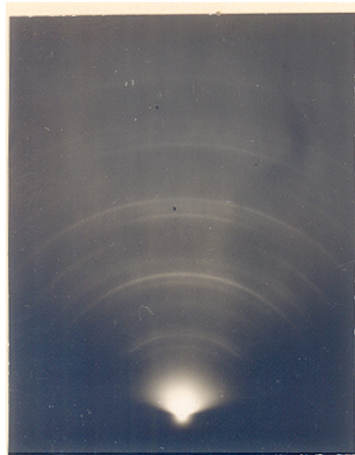


Figure 9.
Electrodeposited
Alpha + Beta Brass



Figure 10.
Electrodeposited
Beta Brass
(100 orientation).

Table 3.

Reflection

Intensity	d/n	hkl values	a
10	2.12 A.	111	3.66 A.
7	1.84	200	3.68
8	1.30	220	3.68
9	1.11	311	3.67
5	1.01	222	3.66
6	1.845	331	3.69
6	0.820	420	3.68

Face-centred
cube

Mean a = 3.68 A.

Alpha brass. a = 3.68 A. as compared with copper a = 3.607 A., which corresponds to a 2% lattice distortion.

Table 4.

Reflection

Intensity	d/n	hkl values	a
9	2.10 A.	110	2.97 A.
8	1.46	200	2.93
10	1.21	211	2.96
5	1.04	220	2.94
7	0.935	310	2.96
9	0.850	222	2.94
10	0.790	321	2.96

Body-centred
cube

Mean a = 2.95 A.

Beta brass. a = 2.95 A. (Theoretical 60/40, a = 2.94 A.)

entirely removed in the pickling process.

Under the microscope, this black oxide appeared to be of a very porous nature and the electron diffraction pattern obtained therefrom showed it to be a mixture of Fe_2O_3 and Fe_3O_4 . (Fig.12).

This porous oxide layer, which had been formed at an earlier stage in the hot-fabrication of the steel, led to the explanation that the easy formation and coalescing of hydrogen bubbles became permissible; there followed a lowering of the hydrogen overvoltage which may be compared with the effect of platinum black on platinum, and a consequent fall in cathode potential around this area. It is known that, in a cyanide brass solution, any lowering of the cathode potential will favour the deposition of zinc in the alloy. Herein lay the explanation of the high zinc brass being deposited on certain of the test pieces. It is important to note further that the interference with the composition of the deposit was not confined to the immediate area of the oxide impurity but that the change was observed at distances away as far as 1 cm.

The observations stressed the need for thorough removal of scale from all components. Apart from interference with the adhesion of the deposit, the variation of the composition of the brass around these areas could allow the zinc content to rise above 40%, to which surfaces rubber would only secure very much reduced adhesion.

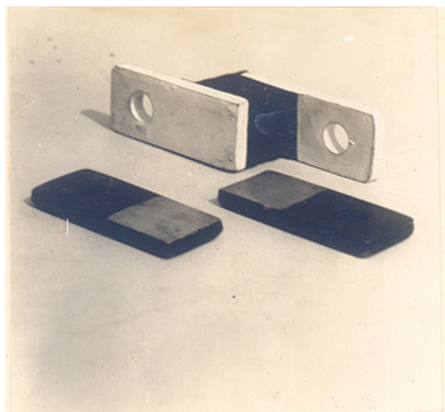


Figure 11. D.50 test pieces.



Figure 12. Fe_2O_3 + Fe_3O_4 .

Table 2.

Reflection.

d/n theoretical Fe_2O_3	d/n observed	d/n theoretical Fe_3O_4
	4.82 A. -	4.85 A.
3.69 A.	- 3.72	
	2.94 -	2.97
2.69	- 2.72	
2.51	- 2.50 -	2.52
2.20	- 2.22	
	2.08 -	2.09
1.84	- 1.84	
1.69	- 1.70 -	1.71
1.60	- 1.60 -	1.61
1.48	- 1.48 -	1.48
1.31	- 1.31 -	1.32

d/n values from oxide film on hot-fabricated steel components - a mixture of Fe_2O_3 and Fe_3O_4 .

Orientation of the Cathode Deposit.

Finch and Sun [48] have shown that when the surface of a cathode is crystalline it may exert a considerable influence on the deposit and may even overcome the tendency of the deposition conditions to control the crystal size and orientation. This influence may persist to thicknesses of 30,000 A. or more.

However in the brass plating process the alpha brass deposit showed hardly any trace of preferred orientation and the grain size was smaller than that of the original alpha iron. If the current density was adjusted to a lower value then beta brass was deposited and the arcing of the rings in the diffraction pattern Fig.10 indicated preferred orientation with the (100) planes parallel to the surface of the substrate. This is usual, since the slower deposition of metal atoms at the cathode allows of a more orderly arrangement of the crystals.

CATHODIC CODEPOSITION

Hillier (loc.cit) had observed that electrodeposited brass from those plating baths which had been in heavy service for some months no longer showed the usual alpha brass pattern but, instead, a new pattern was apparent either together with the brass or on its own.

It was not found possible to identify this rather complex pattern from its derived interplanar spacings but it was discovered that the substance could be removed from the surface by washing in a dilute solution of sodium cyanide, the pattern being once more that of alpha brass. From the sequence of these operations the unknown pattern was named the 'C' pattern and this name is retained for the further experimental work described in this thesis.

Experimental.

The most pressing question was whether the presence of this material, in or on the brass, which gave rise to the 'C' pattern, resulted in any reduction of the subsequent rubber/metal adhesion.

Therefore twelve D.50 blanks (as shown in Fig.11) were plated from a sample of a works bath which was known to be depositing the 'C' pattern. These test pieces were identical and were plated simultaneously. A confirmatory electron diffraction examination showed that the entire surface was covered with substance 'C' (Fig.13), though to the eye the deposit had the normal canary yellow colour of 70/30 brass.

Six of these blanks were dipped for 30 secs. in a N. solution of sodium cyanide, rinsed in distilled water and acetone dried. This treatment removed all traces of

substance 'C', to yield a surface diffraction pattern of alpha brass (Fig.15).

All twelve samples were bonded to a standard rubber stock at 140°C. for $\frac{1}{2}$ hour. The other metal section for each bonded test unit was a similar D.50 blank plated with alpha brass. When cool, the test units were pulled at constant rate of extension on an Avery tensile strength machine until the joint failed. The action of this machine on such a unit is a complex sum of tension, shear, and tear at the rubber/metal interface. The force required for rupture is not therefore a true measure of the tensile strength of rubber/metal bond per unit area (which figure moreover would have little practical significance) but the results obtained on similarly fabricated objects, utilising the same rubber-stock, give an excellent relative indication of the bond strength.

Results and Conclusions.

TABLE 1.

Force required for rupture; lbs./sq.in.			
UNDIPPED.		DIPPED.	
A.	985	G	10400
B.	1020	H	1100
C.	920	I	975
D.	935	J	1010
E.	915	K	990
F.	920	L	985
MEAN	950	MEAN	1020

The above figures gave a definite indication that the codeposition of substance 'C' with the brass resulted in a reduction of possible rubber/metal adhesion, approximately in the proportion of 7%.

Having established that substance 'C' was detrimental, further investigations as to its nature and occurrence were of interest.

Experiments were therefore performed in order to gain information on the chemical nature of 'C', the method being to apply various reagents to the contaminated brass surfaces and to observe any changes thereto by electron diffraction examination.

Experimental.

The usual test pieces, which were shown to give rise to the 'C' pattern, were immersed in the following reagents for one minute.

- A. N. NaCN
- B. N. NaOH
- C. N. CH_3COOH
- D. N. H_2SO_4 and N. HCl.
- E. Boiling distilled water.
- F. A test piece was heated in air to 300°C .
for twenty minutes.

Results.

Complete removal of 'C' was ^{checked} by (A) the sodium cyanide and (B) the sodium hydroxide; (C), acetic acid, produced no change; the mineral acids (D) etched the surface to give rise to ill defined diffraction patterns; boiling water (E) caused no change and likewise the heating to 300°C. was without effect.

From these results it was observed that substance 'C' was relatively stable and soluble with ease only in alkali. The stability to heat and insolubility in water denied the possibility that the material might be a sodium-copper or sodium-zinc cyanide (on which X ray data is inconclusive), the codeposition having arisen from some cathode concentration effect.

It was considered that further light might be thrown on the nature of substance 'C' if more were known about the exact conditions which were responsible for codeposition.

Experimental.

A laboratory scale electroplating cell was set up, consisting of a 5-litre glass accumulator jar partially immersed in a thermostatically controlled water bath. A fully variable current supply was made available from 6 volt car batteries and the anodes were of 70/30 rolled sheet brass.

Samples of the various works electrolytes were obtained and employed successively, under the established conditions, in this cell. It was observed that some electrolytes gave a surface deposit with a 'C' or 'C' + alpha brass pattern whereas others gave that of alpha brass alone. An inspection and analysis showed that those solutions giving rise to a 'C' pattern were characterised by:-

- a. A slight white turbidity.
- b. A higher iron content.

The first characteristic immediately suggested that the material giving rise to the white turbidity might in itself be responsible for the 'C' pattern. Therefore a sample of liquid was removed from a turbid bath and the suspension was found to settle out in a period of 12 hours. The sediment was too fine for filtration and washing by decantation was attempted; it was found however that the removal of the originally present soluble ions brought about peptization of the semi-colloidal suspension with the result that subsequent sedimentation became extremely slow. This rate was increased by the prolonged use of a centrifuge and finally an aqueous suspension of the material was obtained. A drop of this suspension was placed on a thin collodion film, supported by a nickel gauze, and the transmission method of electron diffraction was applied.

The diffraction pattern so obtained was the 'C' pattern identical with that given by the grazing incidence method from contaminated brass surfaces; the identity of the codeposit with the material causing turbidity was thus established.

It was thought that electrophoretic effects might be responsible for the mechanism of codeposition at the cathode. But an investigation of the electrophoretic properties of the suspension in a conventional U tube apparatus showed that such an effect could not be responsible since the particles moved towards the positive electrode, showing themselves to possess negative charge. Therefore the observed cathode codeposition was a case of mechanical inclusion from the suspension; however the fact that the particles possessed a negative charge indicated that some interesting effects might be expected at anodes. Investigations concerning this are described later.

A further quantity of substance 'C', obtained as before, was qualitatively analysed with the following result:-

Major Constituents.	ZINC and FERROCYANIDE.
Minor Constituents.	AMMONIA.
Traces.	Sodium and Copper.



Figure 13.
'C' Pattern
from contaminated
Brass Surface.

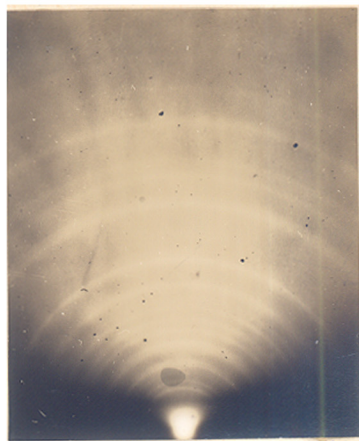


Figure 14.
'C' Pattern
showing also
underlying
Alpha Brass.

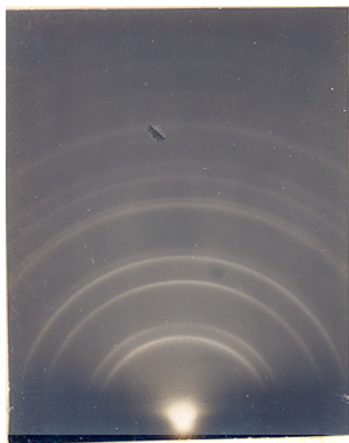


Figure 15.
Alpha Brass.

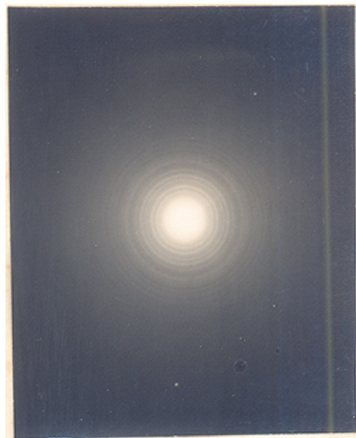


Figure 16.
Zinc Ferrocyanide.

Qualitative analysis was not performed at this stage because of uncertainties in the preparation of (a) a pure and (b) a dry sample. It seemed likely that 'C' was zinc ferrocyanide, which would explain the previously observed fact that plating baths with higher iron contents gave rise to the 'C' pattern. However the diffraction spacings of 'C' showed no agreement with those as published for zinc ferrocyanide and the issue was further complicated by the fact that the spacings obtained from zinc ferrocyanide, both the commercial product and that prepared by the author, agreed with neither of the above. Before discussing this further it will now be convenient to review the available information regarding zinc ferrocyanide and related compounds.

LITERATURE SURVEY OF FERROCYANIDES OF ZINC.

The ferrocyanides of zinc were first investigated at the beginning of the present century, in the effort to explain uncertainties in the ferrocyanide titrimetric estimation of zinc. This operation is dependent upon the formation of an insoluble complex, assumed at the time to be zinc ferrocyanide, with the consequent removal of ferrocyanide ions from the solution by the zinc. The N point, being the first appearance of excess ferrocyanide, was determined by an external indicator (potassium ferricyanide).

It was soon realised that the quantity of standard ferrocyanide taken was not always stoichiometrically in proportion to the amount of zinc required by the reaction:

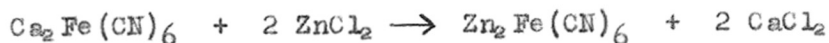


and the titration was generally standardised against a known zinc solution.

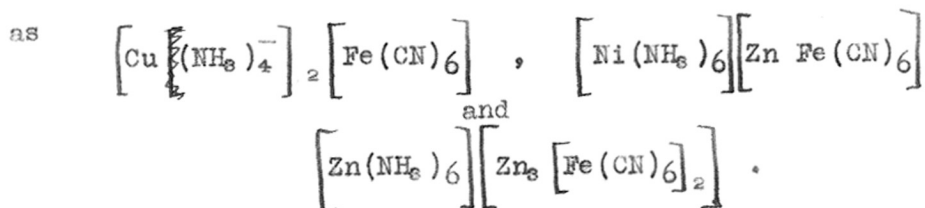
It was shown [50, 51, 52] that the formation of the double alkali ferrocyanide took place simultaneously with the simple ferrocyanide, the relative proportions being governed by the pH, concentration, temperature, etc. of the zinc solution. Various methods were proposed to produce a standard precipitate; one successful method was to have present a large excess of potassium chloride in order to ensure the formation, during titration, of only the double ferrocyanide. Even this method needed a small correction factor and preliminary titration was carried out against a standard zinc solution.

Following from separation of metals earlier in the groups than zinc, ammonium ions were often present in the solution to be estimated, and these caused further interference with the composition of the precipitate. Miller and Falk [51] reported that the precipitate in such a case had the composition $\text{Zn}_{15}(\text{NH}_4)_8 \text{K}_2(\text{Fe}(\text{CN})_6)_{10}$ but Waring [52] found the more simple composition $(\text{NH}_4)_2 \text{Zn Fe}(\text{CN})_6$ in some of his experiments.

H.E. Williams [53] stated that pure zinc ferrocyanide was best prepared by the reaction in solution of calcium ferrocyanide with a large excess of zinc chloride:



If, however, a large excess of sodium or potassium ferrocyanide was substituted for the calcium salt, then the corresponding double alkali zinc ferrocyanide was precipitated. By this method were prepared the two compounds analysed as $\text{Zn}_3\text{K}_2 \left[\text{Fe}(\text{CN})_6 \right]_2 \cdot 28 \text{H}_2\text{O}$ and $\text{Zn}_3\text{Na}_2 \left[\text{Fe}(\text{CN})_6 \right]_2 \cdot 4 \text{H}_2\text{O}$. Treadwell and Chervet disputed this [54], reporting that both potassium and rubidium ions formed a double zinc ferrocyanide but that sodium definitely did not. They warned that potassium ferrocyanide must be used in the standard zinc titration rather than the sodium salt to measure the formation of this double precipitate $\text{Zn}_3\text{K}_2 \left[\text{Fe}(\text{CN})_6 \right]_2$. Reihlen and Zimmerman [55] made a study of many complex cyanides with particular reference to their compounds with ammonia. By washing many ferrocyanides with aqueous ammonia or treatment with gaseous NH_3 , ammines were produced of such constitutions



They also considered that water could exchange for ammonia to some degree. Their researches confirmed the earlier statement of Williams (loc.cit.) that zinc ferrocyanide was converted to a white, very insoluble, ammoniacal compound by means of dilute NH_4OH .

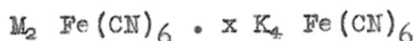
In addition to the researches described above, many other papers appeared relating to zinc ferrocyanide. Many painstaking analyses were performed on the various precipitates only to produce further elaborate and unexplainable formulae to suit these results. Later investigations have shown that the complicated answers obtained can be explained as follows.

1. The failure to analyse homogeneous materials.

Most of the precipitates were colloidal and their ease of peptization made them exceedingly difficult to wash. The high surface area introduced great complications because of the adsorption of foreign ions; the gels precipitated from dilute solutions of zinc ions with ferrocyanide solution absorb the common multivalent anion so very strongly that precipitation is incomplete on mixing equivalent proportions of the two salts. To quote the words of Button and Dodd [56] who re-investigated the problem by electrometric means:".... only in a few instances are normal alkaline earth ferrocyanides precipitated, the precipitate containing alkali ferrocyanides partly by chemical combination and partly by adsorption by these very highly colloidal precipitates

analysis of the various precipitates was of little use since they were colloidal and became peptized before they could be washed entirely free from entrained substances

Their final conclusion was that a general formula for these precipitates was:



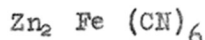
where $x < 1$

2. Incomplete dehydration of the materials.

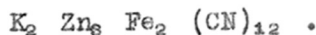
It has recently been shown [57] that all the water present in these gels is adsorbed and that no hydrates are formed; the gels are dehydrated completely in vacuo, there being no steps in the V.P./time curve.

3. Confusion regarding the true formula of zinc ferrocyanide.

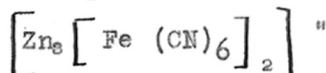
Zinc ferrocyanide has the normal composition:



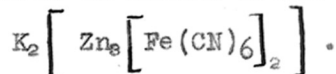
but it reacts with excess $K_4 Fe(CN)_6$ to give a product with an apparent composition



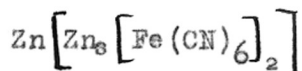
No further zinc is replacable by potassium. We are therefore dealing with a supercomplex anion



which can combine with an alkali metal to form, for example,



A zinc ion can alternatively replace these two potassium ions to form



which formula is the true representation of zinc ferrocyanide, one atom in four of zinc being replacable providing that steric factors will permit.

In 1937 Fordham and Tyson [58] showed, with the aid of electron diffraction, that the various ferrocyanide precipitates which had uses as semi-permeable membranes were truly crystalline though they had previously been considered amorphous when examined by X rays; the shorter wavelength associated with an electron beam enables better resolution to be obtained from very small crystals.

Rigamonti [59] undertook an X ray and electron diffraction investigation of many simple and double ferrocyanides, finding that many compounds of this type, including $\text{Cu}_2 \left[\text{Fe}(\text{CN})_6 \right]$ and $\text{K}_2 \left[\text{Zn}_6 \left[\text{Fe}(\text{CN})_6 \right]_2 \right]$ were isomorphous, the structure being cubic with $a = 10.0$ A. or thereabouts. Zinc and cadmium ferrocyanides were of lower symmetry types to which he was unable to assign structures. Weiser, Milligan and Bates [60] later confirmed much of this showing that the single and alkali ferrocyanides of Cu, Co, Ni and Mn were of an isomorphous face-centred cubic type with $a = 10.02$ A to 10.66 A.; they considered that the ionic

radius of the metal ion was the determining factor for its inclusion in the ferrocyanide lattice, the upper limit being cadmium $r = 0.97$ A. However, zinc ($r = 0.83$ A.) remains an outstanding anomaly and to which they omit all reference.

IDENTIFICATION OF SUBSTANCE 'C'.

The spacings derived from the electron diffraction patterns given by substance 'C' did not correspond with:

- a. Zinc ferrocyanide as quoted by Hanawalt, Rinn and Frevel [61].
- b. A cubic structure $a = 10.0$ to 10.6 A. as to be expected from a double ammonium or sodium ferrocyanide.

It was found however that a precipitate could be obtained which gave, by electron diffraction, a clear 'C' pattern (Fig.17); this product resulted when a solution of zinc salt was allowed to react with either sodium, potassium or ammonium ferrocyanide in the presence of ammonium hydroxide.

The same product was obtained whether zinc or ferrocyanide ions were present in excess, but ammonium hydroxide was essential; sodium hydroxide did not behave in this fashion.

These observations offered two suggestions for the composition of substance 'C'

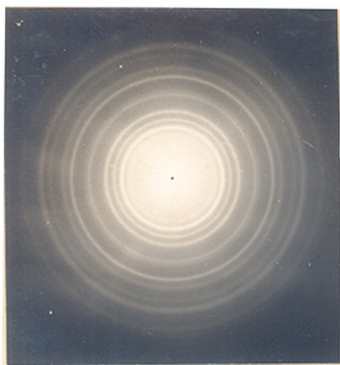


Fig. 17.
'C' pattern from
synthetically
prepared material.

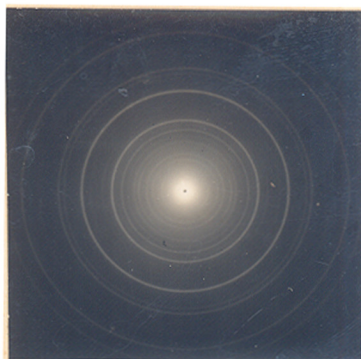


Fig. 18.
Zinc ferrocyanide
co-precipitated with
sodium chloride for
standardisation.



Fig. 19.
X-ray pattern from substance 'C'



Fig. 20.
X-ray pattern from zinc ferrocyanide.

Either

- A. Ammonium Zinc-Ferrocyanide



or

- B. An ammine wherein ammonia coordinates with some of the zinc atoms of zinc ferrocyanide.

The alternative (A) did not appear acceptable because it would be expected to have the face-centred cubic structure which Rigamonti showed as being common to the series. Furthermore (A) is more soluble than zinc ferrocyanide, whereas 'C' was known by experiment to be considerably less soluble than this latter.

Since electron diffraction had shown a method of preparing 'C' under laboratory conditions a quantitative analysis was now capable of furnishing further information. Hitherto this had not been practicable since a sample of 'C', obtained from the suspension in an industrial electroplating bath was unavoidably contaminated with other suspended and adsorbed impurities.

A quantity of 'C' was prepared for analysis as follows:

To 500 ml. of water containing 20 g. ZnSO_4 were slowly added 500 ml of water containing 20 g. $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ together with 80 ml. .880 NH_4OH . Both solutions were at

approximately 80°C. The precipitate was allowed to settle and washing was performed by decantation. The later stages required the prolonged use of a centrifuge owing to extreme peptization of the precipitate. The final product was dried at 60°C. at 1 mm. pressure for one week.

The final analysis was as follows:

Zn..... 35.10%
Fe (CN)₆..... 53.01% (Derived from Fe content)
NH₃ 12.00%

This composition corresponded with that of the product described by Reihlen and Zimmerman (loc.cit.):



which has the theoretical composition:

Zn..... 33.22%
Fe (CN)₆..... 53.83%
NH₃ 12.96%

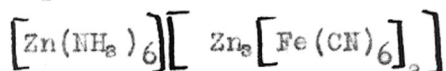
It is considered that the slight difference in composition is attributable to difficulties in preparing a pure sample of 'C'. Two likely factors are the presence of traces of simple zinc ferrocyanide and loss of ammonia in the rigorous but necessary drying. The first factor is substantiated by the observation that, if zinc ferrocyanide was shaken for a few

minutes with aqueous ammonia, then the electron diffraction pattern changed to that of the 'C' pattern. Chemical analysis of the products gave compositions intermediate between the two compounds, an example being:

Zn..... 35.82%
Fe(CN)₆..... 54.72%
NH₃..... 9.46% (by difference only)

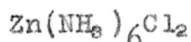
The change in composition was evidently limited to the outer surface of each zinc ferrocyanide granule, the diffraction patterns being the result of surface diffraction from a large number of such granules.

This compound

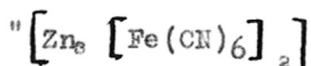


which may be termed a zinc hexamine zinc ferrocyanide supercomplex can therefore be held to be identical with the previously unidentified substance 'C'.

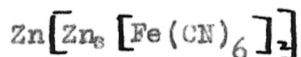
Ammine of zinc salts are well recognised, wherein ammonia co-ordinates with some or all of the zinc atoms to attain a structure of higher symmetry or stability than would otherwise be obtainable. There is, for example, hexamine zinc chloride



but in the case under consideration we have also a supercomplex anion



which in the presence of zinc cations can form the ordinary salt



which is zinc ferrocyanide.

Co-ordination of ammonia around this zinc cation then gives rise to the supercomplex ammine



With a deficiency of ammonia, tetra- or lower co-ordinated ammine might be expected.

Further attention was now directed to the crystallography of this material. The lattice spacings which had been obtained by grazing incidence electron diffraction from contaminated surfaces and transmission through the synthetic product were consistent; but it was difficult to assign indices with certainty by means of the Hull-Davey Nomogram method. Single crystals could not be prepared, there being no solvent which would not change the nature of the material.

However it was suspected that some of the lines on the electron diffraction pattern might actually have resulted from two or more very close diffractions. An X-ray examination by the Hull-Debye-Scherrer method was made*

* Kindly carried out by Mr Rooksby of G.E.C.

Table 5.

ELECTRONS.

X - RAYS.

Intensity	d/n	Intensity	d/n	hkl values (hexagonal system)
6	6.42 A.	faint and ill defined	6.50 A.	100
			5.94	001
8	4.37	10 diffuse	4.39	101
10	3.75	10	3.751	110
8	3.23	6	3.246	200
		4	3.170	111
9	2.84	8	2.847	201
		6 diffuse	2.699	102
		4	2.324	112
9	2.25	8	2.266	121
		4	2.191	202
6	2.14	5	2.163	300
		3	2.033	301
		3	1.890	103, 122
8	1.85	8	1.873	220
		3	1.745	302
6 diffuse	1.72	4	1.721	131
		3	1.691	203
7	1.53	5	1.539	123, 132
6	1.43	4	1.445	104, 231
		4	1.416	402

Comparison of X-ray and electron diffraction values for
 $[\text{Zn}(\text{NH}_3)] [\text{Zn}_6 [\text{Fe}(\text{CN})_6]_2]$, i.e. substance 'C'.

hexagonal $a = 7.496$,

$c = 5.940$.

on some of the prepared powder in the expectation that the somewhat greater angular resolution obtainable by X-rays would separate any multiple lines.

This proved to be the case (Fig.19) and a series of d values was obtained which corresponded well with the electron diffraction values, there being in addition, however, some lines not before resolved.

The diffractions could now be indexed on the basis of a hexagonal structure

$$a = 7.496 \text{ \AA.} \quad c = 5.940 \text{ \AA.}$$

As mentioned earlier, the lattice spacings derived by electron diffraction for zinc ferrocyanide (Figs. 16 and ~~20~~¹⁸) bore no agreement with the only one published series of spacings [61] for this substance obtained by X rays. In view of the fact that the preparation of zinc ferrocyanide is not as straightforward as might appear and also because the material is referred to as $\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, and such a hydrate does not exist, it seemed likely that these published values might be incorrect.

Consequently zinc ferrocyanide was prepared by reacting in solution a large excess of zinc chloride with calcium ferrocyanide. Both this and the commercially obtained material gave the same pattern by electron diffraction examination (Table 6). The small rings indicated a large and complicated unit cell and it was found impossible to assign indices.

By way of confirmation, a further sample was submitted to an X-ray analysis*. The resulting X-ray pattern was not very sharp (Fig.20), but the derived spacings agreed well within experimental error with the electron diffraction values; there was again no resemblance to the published values. It must therefore be concluded that these are incorrect, the X-ray examination having confirmed that to which electron diffraction first drew attention.

OCCURRENCE AND EFFECT OF FERROCYANIDES.

The nature of 'C' having now been established, it became urgent to investigate the circumstances of occurrence and effect of ferrocyanides in the plating and bonding processes.

(a) Occurrence.

As described earlier, the codeposition of 'C' was known to reduce rubber to brass adhesion. Action was very necessary to prevent this phenomenon; moreover it later transpired that ferrocyanide was very detrimental to the process in other ways.

It was obvious that iron salts were finding their way into the plating baths, there to react with sodium

* Kindly performed by Mr Bromelle of B.A.C.

Table 6.

X - R A Y S.		Electron Diffraction	
Intensity	d/n	d/n	Intensity
3	8.56 A.	8.56 A.	6
5	6.20	6.18	7
8	5.47		
10	5.20	5.18	9
7	4.45		
8	4.26	4.32	6
7	4.03	4.08	7
10	3.89	3.90	8
6	3.59		
7	3.49	3.46	6
5	3.34		
6	3.01	2.98	5
6	2.89		
7	2.62	2.73	7 diff.
5	2.44	2.42	7

Table comparing d values for zinc ferrocyanide by X ray and electron diffraction methods.

cyanide to form ferrocyanide. The continual hydrogen gassing during the operation prevented oxidation to ferricyanide. An examination of the plating shops revealed these possible sources of contamination.

- a. Exposed iron in the electroplating tanks and heating coils.
- b. Iron present in the commercial salts employed in preparing and maintaining the electrolyte.
- c. DRAG-IN of iron through insufficient washing after pickling steel or cast iron objects.

Also the adherence of small particles of iron after the wet scratch-buffing of such objects as cast-iron track wheels for Bren carriers.

Source (b) was not at the time considered significant but it was recommended that an occasional check be made. Source (a) was preventable by good maintenance of the rubber linings. Source (c) required the most attention; freshly cleaned components were stored in a large iron tank, containing 5% sodium cyanide, immediately prior to brass plating. Analysis of this liquid showed a high iron content and observation of the process revealed that the components were lifted out of this tank directly into the plating bath, each operation transferring iron into the latter.

The following figures illustrate that 'drag-in' of the standing tank liquid was causing introduction of iron

	Iron (as g. $\text{Fe}(\text{CN})_6$ per litre)
Bath I (New)	2.90
Bath II (Old)	11.25
Standing tank liquid	48.10

The recommendation was therefore made that the washing process be improved.

b. Effect of Ferrocyanides.

A search through the literature revealed only one mention of the effect of ferrocyanides in cyanide electroplating solutions [62], namely that silver plating baths often contained ferrocyanide and this severely interfered with the estimation of uncombined cyanide through premature precipitates being formed during direct silver nitrate titrations.

Experiments described earlier had shown that colloidal substance 'C', if present, was mechanically deposited on the cathode from a brass plating solution; this in turn effected rubber/brass adhesion. In view of the fact that the particles had been found to possess a negative charge it appeared that electrophoretic interference at the anode also was likely to occur.

Experimental.

To a Coats brass plating solution (Cu 26.2 g.p.l.; Zn 13.0 g.p.l.; Uncombined cyanide 10.0 g.p.l.; pH 10.9; and

some ammonia), was added sodium ferrocyanide to give a ferrocyanide content of 12 g.p.l. Slight turbidity occurred. Straightforward cell-voltage/anode-current-density readings were obtained. A sudden rise in the curve at 20 ma./sq.in. indicated the formation of some protective film. When further powdered 'C' was added to the solution, the anode film appeared at a current density of less than 10 ma./sq.in. An electron diffraction examination of this film in both cases revealed the 'C' pattern.

The two factors encouraging this film formation were:

- a. The lowering of pH in the immediate vicinity of the anode, with precipitation of 'C'
(The "Bedeckungspassivitat" of Muller).
- b. Anaphoretic migration of colloidal 'C'.

In the case of an iron free sample of the original solution anode passivity first set in at 36 ma./sq.in. The diffraction pattern was indistinct but is quite likely to have been due to zinc cyanide, formed according to the first of the factors mentioned.

At this stage in the investigation a general paper was published by Clarke, Bradshaw and Longhurst [63] on brass plating. They stated here that the presence of ferrocyanide caused a large reduction of anode efficiency, and they noticed a film on the anodes which they suggested might be zinc or copper ferri or ferrocyanides. It appears extremely likely that this film was identical with that just described, being

the zinc hexamine zinc ferrocyanide. In addition to ferrocyanide, ammonia is necessary for the formation of this substance, but this solution contained 3 ml. .880 NH_4OH per litre added besides ammonia invariably present through cyanide decomposition.

In the same report, the above authors drew attention to the fact that ferrocyanide dissolved in the electrolyte limited the usefulness of certain methods of uncombined cyanide determination. With reference to this, the effect appeared to be even more serious in some cases under present consideration where the plating bath solutions contained quantities of the suspended complex.

The following experiment confirmed this; a sample was taken of a works electrolyte which was several months old but still in use. As withdrawn, the liquid had a milk-like consistency. A measured volume was analysed and a second analysis upon the clear supernatant liquid which resulted when this solution was allowed to settle for 24 hours.

A. Sample turbid as removed.

Cu 21.52 g.p.l. Zn 12.38 g.p.l. $\text{Fe}(\text{CN})_6$ 21.22
g.p.l.

B. Supernatant liquid after settling 24 hours.

Cu 21.08 g.p.l.; Zn 5.15 g.p.l.; $\text{Fe}(\text{CN})_6$ 4.11 g.p.l.

The uncombined cyanide was not determined, but ^{the discrepancy} would have been at least equally as great since the zinc content enters into the calculation of the above.

These results demonstrated that the presence of suspended 'C' in the brass plating bath could invalidate daily routine analysis, there being a dependence on the state of the sample taken for this analysis. By standardising the method of withdrawing samples, results of use relative to each other could be obtained but this was hardly satisfactory. The recommendation was therefore made that the suspension be removed by a temporary lowering of pH followed by filtration or sedimentation or in extreme cases that the electrolyte be discarded.

CHAPTER III.

AN ELECTRON DIFFRACTION EXAMINATION OF THE BONDING
PROCESS.

The preceding chapters have emphasised the process of brass plating but it is of equal interest to consider the nature of the rubber/metal bond and the proven superiority of alpha brass in attaining this.

This field has been little investigated, information being mainly limited to a realisation that sulphur must play some essential part in promoting the adhesion. If electron diffraction could be applied to an examination of the adhesion, then useful results were to be hoped for.

Experimental.

Some D.50 units were pulled to destruction in an Avery testing machine. Attempts to examine the exposed surfaces by electron diffraction were fruitless; the separation of rubber from metal was not sufficiently clean and ridges of the former remained on the metal. By subjecting further test units to a very rapidly applied force, somewhat cleaner

fractures were obtained but the surface was still not suitable for diffraction.

If, however, the units were immersed in liquid nitrogen, it was found that a shearing action produced a clean cut separation between rubber and metal. A visual examination of the exposed surfaces revealed a normal appearance for the rubber but a green iridescent film on the brass. Such a surface was submitted to an electron diffraction examination and gave a clear pattern (Fig.21).

It was further found that a quite similar pattern (Fig.22), only more distinct, was given by the surface of alpha brass which had been exposed above rubber in an open vessel at 160°C. for $\frac{1}{2}$ hour. The derived spacings (Table 7) corresponded with those of hexagonal cupric sulphide (covellite).

This experiment therefore gave definite proof that the adhesion of rubber to brass results from an intermediate cupric sulphide layer, produced during vulcanisation. The bright green interference tint of the interlayer suggested a film thickness of the order of 1,000 A.

Although these patterns gave sufficient lines for identification as cupric sulphide, it was advisable to compare them with a reference pattern. It was decided to precipitate cupric sulphide by passing hydrogen sulphide into a weak cupric acetate solution at room temperature. However

if hydrogen sulphide were merely blown across this latter solution, then a brown sulphide film was produced on the surface, which prevented further reaction; this film was eminently suitable for the transmission method of electron diffraction and was removed and washed in the normal fashion. Contrary to expectation the pattern obtained (Fig.28 and Table 8) was not that of hexagonal cupric sulphide.

If this film were heated in an air-oven to 90°C., a transition took place, giving rise to an extremely clear pattern of hexagonal cupric sulphide (Fig.29); this pattern was likewise produced (Fig.30) by passing the hydrogen sulphide over cupric acetate solution heated to 90°C. By a process of elimination, the transition temperature was found to be about 75-85°C.

The spacings of the low temperature form did not correspond with any simple structure. Nor did they bear any relation to published spacings for cuprous sulphide, Cu_2S , or digenite $\text{Cu}_{1.8}\text{S}$, although it must be borne in mind that values for such are very confused, various authors having together allotted a total of nine different structures for cuprous sulphide between 0° and 120°; the cubic CaF_2 type of structure quoted for Cu_2S in many text-books applies only to the material prepared at above 300°C.

It would therefore be unwise to make a definite

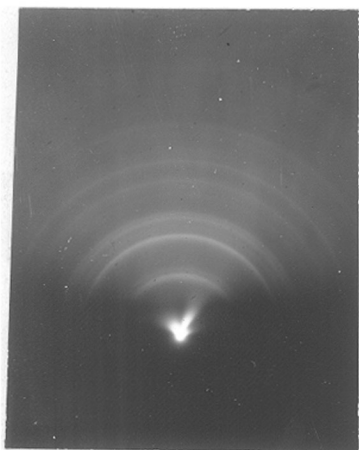


Fig. 21.
Action of rubber on
alpha brass at 160°C.,
giving pattern of
cupric sulphide.

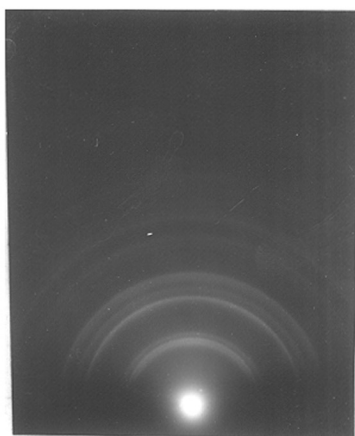


Fig. 22.
Cupric sulphide produced
by exposure of alpha brass
to sulphur vapour at 160°C

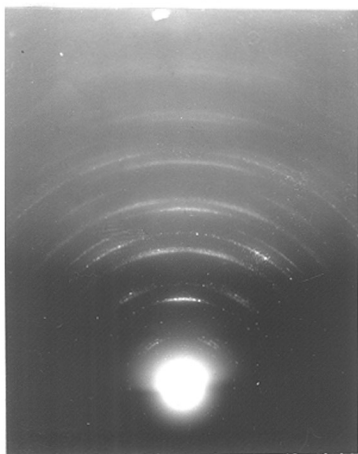


Fig. 23.
(001) oriented and
macrocrystalline cupric
sulphide resulting from
action of sulphur on
copper at 160°C.



Fig. 24.
macrocrystalline cupric
sulphide resulting from
action of sulphur upon
alpha brass at 250°C.

Table 8.

Transmission.

Intensity	d/n.
9	3.29
6	3.16
8	2.40
8	2.23
9	2.01
8	1.94
6	1.85
9	1.72
7	1.66

Spacings of cupric sulphide prepared at 25°C.

statement about this unidentified sulphide pattern, though it seems reasonable to suggest that it is a low temperature form of cupric sulphide. It is worth mentioning that this method of preparing an electron diffraction specimen is very useful and the author hopes to apply it to the study of some other metal sulphides and selenides.

Referring back to the action of sulphur upon brass, it was of interest to compare the action upon a copper surface, since it was hoped from these investigations to provide some answer to the often asked question -- "Why brass but not copper".

Therefore D.50 steel blanks were plated from cyanide solutions with alpha brass (70/30) or copper and exposed above sulphur at 160°C. for half an hour - this temperature and time were chosen so as to conform with those of vulcanisation. The effect, which was also no different when hydrogen sulphide was employed, was as follows: The film produced on the brass was the transparent, unoriented microcrystalline cupric sulphide as in Fig. 21 or 22. That upon the copper showed several differences; the cupric sulphide was a relatively thick black lustrous film and the diffraction pattern (Fig.23) showed larger individual crystals in pronounced (110)

orientation. To produce a similar film upon brass was found to require temperatures of 250°C. or 300°C.

(Figs. 24 and 26). Conversely, the thin, unoriented microcrystalline cupric sulphide characterised on brass at vulcanisation temperatures was formed on copper at only 100°C., and even then some orientation was evident (Fig:25). Low zinc brasses were found to give intermediate results, as was to be expected.

From these observations it was evident that the entrance of zinc into the copper lattice, in the simple solid solution of the alpha phase, could have a considerable influence in reducing the reaction rate of the alloy with sulphur.

This has been demonstrated before - Vernon [64, 65] observed it in his gravimetric experiments. A close analogy is the addition of cadmium to silver to render it non-tarnishing in a sulphur atmosphere. Bauer and Arndt [66] showed that zinc, tin and aluminium when added to copper each reduced progressively the susceptibility to sulphur corrosion.

It is to be noted that these metals are in themselves comparatively unreactive with sulphur but, in proportion, their inhibiting effect seems to be greater than their atomic percentage in the alloy.

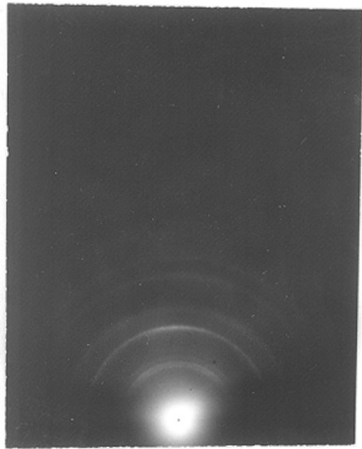


Fig. 25. Cupric sulphide resulting from sulphur attack on copper at 100°C. (Some evidence of (001) orientation).



Fig. 26. Macrocrystalline cupric sulphide from action of sulphur upon brass at 300°C. (Reflection pattern, but projecting flakes at lower edge throw a pattern behind the shadow edge.



Fig. 27. "Reflection" pattern from projecting flake upon a copper surface exposed to sulphur at 160°C. The pattern results from transmission through the basal planes of hexagonal cupric sulphide.

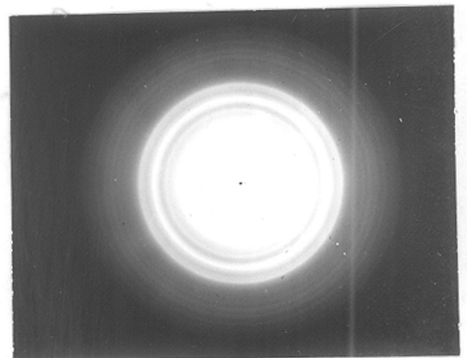


Fig. 28. Another form of copper sulphide produced by blowing across a cupric acetate solution at 25°C.

The reasons for this progressive reduction of corrosion are attributable to two factors:

A. Modern theories (see, for example Wegener [67] and Pfeil [68]) hold that the surface reactions of metals have their ultimate velocity governed by the diffusion of the metal through the film of reaction product rather than vice versa as was originally considered.

Zinc is relatively inert to sulphur attack at temperatures under consideration and the reaction and film formation is dependent upon a supply by diffusion of copper. The presence of zinc in the alloy, which in the alpha phase substitutes at random for copper, must reduce the amount of copper available for this diffusion and this is accentuated by the fact that zinc is readily the more diffusible of the two. The cessation of reaction after a thin film has been formed on 70/30 brass could be explained by the "sealing" of this cupric sulphide film with zinc.

B. The reaction $\text{Cu} \rightarrow \text{CuS}$ involves a volume increase on the surface of almost 2:1. Finch has pointed out [69] that a change of dimensions during a surface reaction (oxidation in this case) could prevent the crystals of the product from packing closely together and protecting the underlying metal.

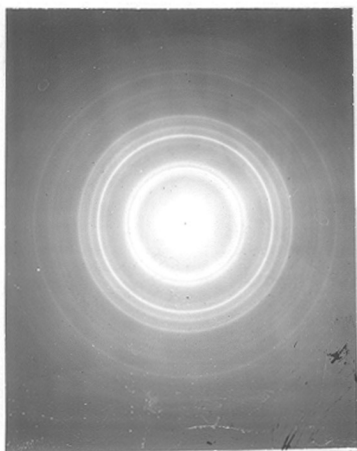


Fig.29. Specimen as in Fig.28 heated to 90°C., transition to c.p.h. CuS.

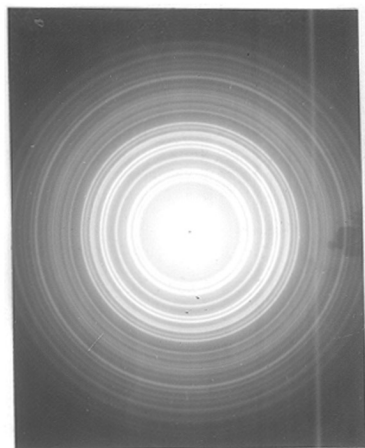


Fig.30. c.p.h. CuS^{*} produced by blowing H₂S across solution of cupric acetate at 90°C.

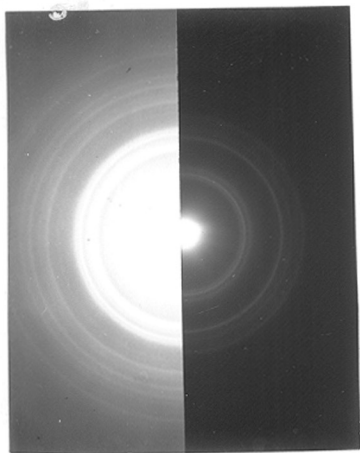


Fig.31. Comparison shutter photo of film produced by blowing H₂S across cupric acetate.
A at 25°C B at 90°C.

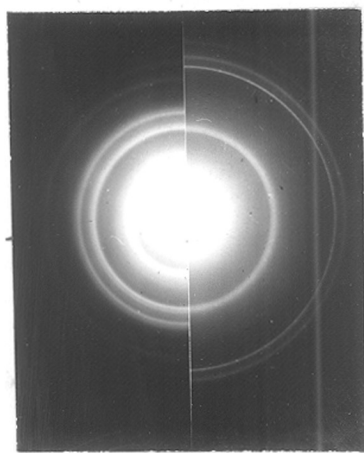


Fig.32. Comparison shutter photo of lower temp. form of sulphide against graphite. (for standardisation).

If, as in our case, the original metal surface was partially composed of inert atoms (zinc) then it is reasonable to assume that at the commencement there will be some room available for this expansion but, in the case of a pure copper surface, a buckled initial film may be expected and this is liable to be pervious to further attack.

It now becomes possible to elucidate some details of the rubber/metal bond.

Adhesion is satisfactorily secured to alpha brass because vulcanisation conditions are such that they produce upon this surface a thin coherent film of cupric sulphide. The adhesion would appear to be truly chemical, there being a gradation in the type of valency linkages from the rubber hydrocarbons via their attached sulphur atoms through the cupric sulphide to the metal; a sharp boundary between polar and non-polar materials is thereby avoided. 70/30 brass was a convenient choice for promoting adhesion because its reaction rate with sulphur was well suited to industrial rubber stocks and the vulcanisation conditions thereof. This does not infer that every rubber is suitable and Gurney [31] and Buchan [32] have studied the effects of moulding conditions, accelerators, anti-oxidants and

softeners. Accelerators must be employed with care and ultra-accelerators are not suitable.

Copper, on the other hand, is attacked too rapidly; the cupric sulphide film is thick and lacks mechanical strength. To produce a film upon copper analogous to that upon brass would require a temperature of about 100°C. or a very low sulphur rubber stock, neither of which is practicable. A further source of weakness, when copper is employed, is betrayed in Fig.23, where marked (110) orientation of the cupric sulphide is apparent - which, incidentally, explains the lustrous sheen of the black film. Now cupric sulphide is a hexagonal plate-like crystal with a very pronounced basal (001) cleavage (cf. mica) and (110) orientation infers that the prism faces lie parallel to the surface and the cleavage planes are perpendicular to it. Any alignment of cleavages is a source of weakness and since, in the extension of a rubber/metal unit, there must be a large component of force resolved also perpendicularly to this surface, the orientation cannot fail but to be detrimental to adhesion.

By the reasoning mentioned previously, it seems likely, although it was not investigated, that a silver/cadmium alloy of the right proportions would bond satisfactorily to a normal rubber. Malone [70] claims copper/tin(bronze)

for this purpose. There is, however, little point in adopting these, since they are not likely to be any easier to electrodeposit than brass, which process, moreover, has the benefit of successful practical experience.

BONDING TO NEOPRENE.

The Neoprene range of synthetic rubbers are characterised by the fact that sulphur is not essential for their vulcanisation, although it is quite often incorporated in the mix.

It was reported privately that a Neoprene mix which contained no added sulphur was yet capable of securing good adhesion to brass when vulcanised in contact. This was confirmed by experiment and therefore appeared to be a direct contradiction to the results described previously which showed the formation of an intermediate film of cupric sulphide.

But when a sample of this "sulphur-free" Neoprene mix was heated in close contact with alpha brass at 160°C., the electron diffraction pattern obtained was an unmistakable example of cupric sulphide (similar to Fig.21) such as was given by sulphur-containing natural rubber mixes.

Therefore sulphur must have been present, though none had been added as such in the compounding, which was as follows:

Neoprene GN	100 parts by weight
Brown Substitute	20
P.33 (Soft Carbon Black)	75
Pine Tar	5
Stearic Acid	0.5
MgO	6
ZnO	1
Nonox S (Antioxidant)	2

The 'Brown Substitute', which is used as an extender in nearly every Neoprene mix, provided the explanation. It was found out that this had a total sulphur content of 22.4%, 3.4% of which was denotable as free sulphur. The actual composition of 'Brown Substitute' is complex and unascertainable but it consists mainly of semi-vulcanised mineral and vegetable oils. Sufficient sulphur was evidently available for the formation of the cupric sulphide adhesive interlayer, and, as far as the author is aware, there have been no successful results in bonding Neoprene to brass where sulphur has not been present in some form.

SUMMARY OF RESULTS.

The experimental investigations have shown that the electrodeposition of brass, required for rubber adhesion, may be attended by certain difficulties.

Firstly traces of unremoved scale on the steel components may cause interference with the composition of the brass. Secondly, and the more important, the presence of iron in the electrolyte can be very detrimental to its analysis, operation, and also to the subsequent bonding process. Iron, which in this case was introduced mainly by drag-in, results in the formation of a highly insoluble, semi-colloidal zinc ammonium ferrocyanide complex. The results of electron diffraction and X-ray examinations of this and associated compounds have been presented.

Electron diffraction has shown that the adhesion of alpha brass to rubber proceeds by virtue of the production of a thin, coherent, intermediate film of cupric sulphide. Copper is unsuccessful for this purpose because the attack by sulphur is too drastic under normal vulcanising conditions, a thick, selectively oriented, mechanically weak cupric sulphide film being formed. Explanations have been offered for this difference in reaction rate.

Neoprenes, which bonded satisfactorily to brass although sulphur had not been added to the mix, have been shown to derive the sulphur necessary for adhesion purposes from other ingredients of the mix.

These researches, by the employment of electron diffraction, have elucidated certain problems in connection with the bonding of rubber to metals. More, however, remains to be investigated in other stages of the process and it is hoped that a stimulus is provided for the application of scientific method and, in particular, the use of modern physical means of investigation, to other relevant problems.

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