ELECTROLYTIC AND CHEMICAL POLISHING

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INTRODUCTION

APART from two or three experiments at the beginning of the century, methods of polishing metallic surfaces by a process of anodic dissolution —electro-polishing or electrolytic polishing—have been known only for the last 25 years. Recently it has been discovered that electric current is not always indispensable, and as a result techniques of chemical polishing have been elaborated, which are limited to certain metallic materials and much less general in their applications.

Progress has been most marked perhaps since the present author first successfully obtained, without the aid of abrasives and traditional materials, a specimen of copper of 1 cm.^{2} area with a surface sufficiently smooth and bright to enable it to be examined under the microscope. Gradually, operating conditions have been established that are applicable to all the metals of technical interest, and to a large variety of their single- or multi-phase alloys. There is no doubt that there does not exist today anywhere in the world a metallurgical or metal-physics laboratory which does not utilize electrolytic polishing either in its simple, primitive form, or in the form of automatic, commercial equipment.

The metallurgist or the physicist is rarely interested in specimens measuring more than about 10 cm.^{2}, but the engineer, who has also learnt to appreciate the value of electrolytic polishing, has succeeded in applying it to machine components as large as the crankshafts of automobile engines and the gears of electric and Diesel locomotives.

The present review deals only with problems relating to the methods of electrolytic and chemical polishing, and excludes their scientific and technical applications. The author believes that, whatever their speciality, all who use, or could use, these modern methods ought to know their experimental and theoretical bases. A widespread belief exists that electrolytic polishing gives a particular type of surface

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(excellent according to those who make use of the process, very unsatisfactory according to those who do not favour it). The real facts are directly opposite to this view, which has, unfortunately, led to many errors of interpretation that have had serious consequences.

The review consists of three parts and an appendix. The first part deals with general topics involved in the definition of the state of a metallic surface. The second part begins with a brief history of the electrolytic and chemical polishing processes, and then deals with the principles underlying them. The mechanisms which have been suggested to explain the effect of polishing are next described and discussed in some detail, for they are important in respect to the properties of the surfaces obtained, and to the development of new techniques.

In the third part, the characteristics of surfaces mechanically, anodically, and chemically polished are compared. This comparison indicates very clearly the reason why electrolytic and chemical processes, sometimes followed by other treatments, are so widely employed today for the preparation of specimens intended for physical and physicochemical study.

The appendices summarize practical data on the technique of electrolytic and chemical polishing, and give corresponding references.

A. DEFINITION OF THE SURFACE STATE OF A METAL

In order to understand the reasons which have led to the considerable development of electrolytic polishing in the fields of science and technology, it is necessary to bear in mind certain principles regarding the state of the surface and its bearing on the properties of metals.

The concept of surface state was first introduced by engineers, which explains why it is generally held to apply only to the characteristics depending on the "microprofile", because these play an essential, though not an exclusive, part in the behaviour of mechanical components. Properly speaking, the term " surface state " should define as completely as possible all the characteristics of the surface; these can be considered under three headings: (1) the microgeometry, which includes the point-to-point variation in cross-section, and therefore covers the dimensions, distribution, and frequency of occurrence of depressions and asperities; (2) physical characteristics, covering the structure on the microscopic, sub-microscopic, and atomic scale, internal strain, and hardness; (3) chemical characteristics, covering the nature and distribution of chemical elements or compounds other than those belonging to the metal itself.

Until recently, each specialist attached importance only to one particular class of surface characteristics. For instance, as mentioned

above, the engineer considered the finish produced by machining, grinding, or polishing; the physicist studied the properties of the metal without paying particular attention to the surface as such, seeking only to produce a specimen in the condition most suitable for his observations; whilst the chemist investigated the amount and nature of the compounds produced during chemical attack or corrosion, with the sole object of establishing the laws governing these processes, and considered the metal as a homogeneous whole, without being greatly concerned whether the surface layers were identical with the mass of metal or not. It is, however, unquestionable that, depending upon the type of phenomena to be studied, or upon the conditions under which the metal surface will be required to operate in service, certain characteristics are of outstanding importance, though there is now ample experimental evidence that other characteristics cannot be deliberately ignored. Moreover, the various factors that determine the surface are liable to affect one another; for example, the production of a desired micro-geometrical finish will affect to a greater or lesser extent the structure and the properties associated with it, such as the hardness and internal stress, to say nothing of chemical contamination with grease, oxides, or foreign matter generally.

Many examples confirm the simultaneous effects of all the various factors that determine surface state, but it will be sufficient to mention the phenomena of abrasion, wear, and oxidation, all of which depend on the finish, structure, and chemical nature of the surface. The effect of the surface state is not solely confined to purely superficial phenomena, because the methods of studying the properties of the material as a whole very often involve, to some extent, the exposed surface. Every time, therefore, that an investigator studies a particular property of a metal, he should consider whether his results do not really apply to a complex system, in which, to an extent more or less easy to determine, the properties of the massive metal and those of the surface both play their part. The lack of reproducibility in some experimental results involving electrolytic, chemical, or optical phenomena on metal in massive form is certainly often traceable to inadequate knowledge of the surface condition.

Polish is one of the most important features of a surface. It is characterized by a smooth and brilliant appearance, obtained by rubbing with an extremely fine abrasive carried on very soft material. Polishing is often only the last of a series of finishing operations performed mechanically, as by milling or abrasion. In industrial applications, polishing is not only an operation designed to give a simple decorative effect, but it also plays an important part in finishing various components. For instance, the techniques of honing, lapping and

super-finishing, which are in effect similar to polishing, are frequently used to improve frictional properties, to reduce wear, and to improve resistance to alternating stress (fatigue).

The polished state is of no less interest in the laboratory. In addition to the usual micrographic examination called for in controlling fabrication processes and in determining equilibrium diagrams, scientific research on problems such as the relation between structure and properties, and changes in structure taking place during the processes of deformation, recrystallization, creep, fatigue and so on all require, at some stage or other, the polishing of test specimens. This polishing has to be done with particular care when electron microscopy is used as the method of investigation, and also when the modern techniques of microhardness, interference, and phase-contrast microscopy are employed.

Polishing is just as necessary in physical as in metallographic investigations, as for instance in problems involving magnetism, surface conductivity, optical and thermal properties, and so on. Sometimes an investigator is content to deal with a surface less perfect than a polished one; for instance, many studies of corrosion and of oxidation have been made on materials finished on emery papers. It is therefore very important to know the microgeometrical, physical, and chemical properties of surfaces abraded and polished mechanically. This matter will be discussed later, because it is instructive to compare these properties with those of surfaces polished electrolytically, and because it appears that electrolytic polishing is a process of great value in studying surfaces worked mechanically, especially in respect of their structure and physical properties. It is necessary to refer to the various techniques for evaluating the characteristics of a metal surface, but a very brief summary will suffice.

I.—Microgeometrical Properties

In general, each method of evaluating the microprofile has an optimum region of sensitivity and precision. Those suitable for surfaces roughly finished by means of tools, as in turning, milling, and cutting, are less suitable for surfaces with a higher degree of finish, such as are produced by polishing, or superfinishing. The boundary between the two groups lies roughly at asperities of the order of 1 micron.

Where the surface roughness is on the average greater than 1 micron, recording profilometers are very convenient.[1] These are electromechanical devices which produce a graph of the asperities and depressions with a magnification between 1000 and 10,000. The distances in the horizontal plane are also recorded on an enlarged scale, but with a

much smaller degree of magnification. To measure surface irregularities smaller than 1 micron, optical devices are employed, of which the best known make use of interference fringes. These techniques, and others also, have the advantage of being non-destructive, which is important in process control, but they give a picture of the surface which requires interpretation. Electron microscopy, using a replica technique (plastics, thin films and evaporated aluminium or carbon), provides a degree of resolution sufficient to reveal asperities of the order of tenths or hundredths of a micron, but the method is too delicate to be employed elsewhere than in a specialized laboratory.

Phase-contrast microscopy is easy to use on any metallographic microscope, and reveals details of the surface that are hardly visible or quite invisible under normal illumination. Very recently, Nomarski and Weill[2] have reported considerable progress with an optical apparatus that makes use of double-beam interference contrast in polarized light. The sensitivity towards microscopic asperities equals that of the method of interference fringes, but has the great advantage that it gives a real image of the surface, showing the details with a resolving power in depth superior to that of phase-contrast microscopy. Applications of this elegant method will be discussed later in connection with electrolytically polished surfaces (p. 181).

A destructive method of testing, often used in the laboratory, and applicable over a wide range, is known as the "taper section" method. It gives the true microprofile directly[3] and is valuable for following changes in the microstructure in the superficial layers.[4]

II.—Physical Characteristics

Structure can be considered on three scales: microscopic, submicroscopic, and atomic. The first two are covered by optical and electron microscopy, respectively, both of which give images corresponding strictly with the surface. The structure on the atomic scale is determined by X-ray diffraction, although owing to the penetration of the radiation into the material, the diagrams obtained reveal the average structure of a layer extending to a depth of possibly 0·05 mm. below the surface. Electrons, being much less penetrating, yield diffraction patterns from a layer of only a few atomic planes thickness, say 10-20 Å. All diffraction diagrams have to be interpreted, and this, particularly in the case of electron diffraction, presents certain difficulties.

The other important physical properties of a surface are hardness and internal strains. As regards the former, only the hardness under very light loads, up to perhaps a few dozen grammes, needs consideration. The measurements are made at specially selected points, which

is a great advantage, and with oblique sections it is possible to study the relationship between structure and hardness in the surface layers.

When metallic surfaces are subjected to machining, or to some other treatment such as shot-peening or vapour-honing, tensile or compressive stresses appear immediately, and these play a great part in determining the behaviour of the specimens under fatigue. Unfortunately, measurements of these stresses are very delicate to make, and often lack precision, so that information about their correlation with other surface characteristics is frequently lacking.

III.—Chemical Characteristics

The main cause of surface contamination is atmospheric oxidation, and hence a study of the chemical characteristics of a surface involves the determination of the composition and thickness of any oxide or oxides that may be formed. In favourable cases, the layer of oxide formed in air can be detached from its metallic support, but in general it is extremely thin and must be studied *in situ*. Where the thickness is at least 15–20 Å., the best and most commonly used method of investigation is electron diffraction. Measurements of solution potential reveal the existence of even thinner layers, but do not serve to measure their thickness or to determine their composition. In the case of copper, electrolytic reduction provides a means of measuring thickness down to 10 Å. and indicates the nature of the oxide.[5] Impurities other than oxides may occur on metallic surfaces, and can be detected and estimated by appropriate microanalytical methods.

B. HISTORY, PRINCIPLES, MECHANISM, AND TECHNIQUES OF ELECTROLYTIC AND CHEMICAL POLISHING

I.—History

1. *Chemical and Electrolytic Attack*

Metals enter more or less readily into solution in acids and only rarely in bases, forming the corresponding salts. Solution is generally accelerated by making the specimen the anode in an electrolyte.

The reactivity of metals towards chemical reagents has been used since the outset of classical metallography to reveal the details of the microstructure of a polished surface. On such a surface the structure is either invisible, or is revealed only by the relief or the intrinsic colour of the constituents. Chemical reagents then function by specifically attacking the separate phases.

Even in the case of a pure homogeneous metal, etching of the polished surface takes place. Its initial stages depend on the physical state of the specimen, and the rate of attack varies according to the crystal orientation and the perfection of the lattice. In general, the boundaries of the crystals and any cold-worked regions are the most susceptible to attack.

Finally, the progressive action of chemical reagents—acids, bases, or salts—is shown by the appearance and development of microgeometrical features on the initially smooth surface, which therefore loses its highly-polished brilliance. The same clearly holds good during anodic dissolution.

2. *Discovery and Evolution of Electrolytic Polishing*

The somewhat elementary facts given above about chemical attack, which have been known for a very long time, helped very little towards the solution of a problem submitted to the author in 1929 by the laboratory of a Company making electronic equipment. The problem was to find a chemical or electrolytic method capable of producing a surface on pieces of pure nickel comparable with that normally obtained by the usual polishing technique. At that time, some men in the shop already knew that pickling brass in an acid bath containing soot gave an unusual brilliance to the surface, while others had noticed that the silver anodes in a plating bath occasionally acquired a satin finish whilst dissolving. These examples did not represent true polishing effects, but such an effect was reported in gold in 1907,[6] in silver in 1910,[7] and much later in stainless steels.[8] These observations had been forgotten, and were unknown to the author at the time his own investigations were begun. It is rather curious to note that the electrolytic polishing of silver was rediscovered in Germany in 1941, and on two occasions, in 1942 and 1946, in the United States.

In collaboration with H. Figour, the author soon found the conditions necessary for polishing nickel, and showed that similar results were possible for other metals (copper, aluminium, iron, molybdenum, lead).[9] Although the process reached an industrial stage for finishing certain nickel and molybdenum parts, it is very probable that it, too, would soon have passed into oblivion. Fortunately, the author was led to undertake systematic researches with a view to the application of electrolytic polishing in micrographic work. The first micrograph made without using the traditional method of mechanical polishing was published in 1935.[10]

This result, obtained on copper, was rapidly extended with great success to other metals and alloys. The electrolytes used comprised

sulphuric, phosphoric, acetic, and perchloric acids in solution in water or ethyl alcohol, and these solutions still form the basis of most polishing baths. From 1935–37 onwards, the author continued to draw attention to the considerable advantages of polishing electrolytically, in speed and quality of surface, for preparing metallographic specimens,[11] but very few metallurgists adopted the process, the remainder criticizing it on the ground that it revealed unusual features! On the other hand, many physicists took very great interest in the process that was capable of producing surfaces without any trace of scratches or structural disturbances, and possessing outstanding advantages for research on oxidation,[12] optical constants,[13] and magnetic properties of metals.[14] Apart from the value attached to the preparation of their specimens, these investigators were interested in the theoretical side of the phenomenon and attempted to determine its mechanism. In this way, Elmore was led to publish the first serious theoretical paper.[15]

The outbreak of hostilities in Europe contributed much to the adoption of electrolytic polishing for preparing metallographic specimens. Lack of money, the poor quality of polishing materials, the shortage of trained staff, and reduced output were all important factors in the development of the process in metallurgical control and research laboratories.

At about the same time industrial applications were first considered. Previously, electrolytic polishing had been used in the workshop only for pure aluminium[16], but during the war the Germans attempted to polish electrolytically certain components of automatic weapons,[17] and in France Mondon,[18] working in the laboratories of the Hispano Suiza Co., perfected his remarkable process of electrolytically superfinishing certain mechanical components.

From the industrial point of view, the most important contribution was made by American investigators at the Battelle Memorial Institute, who, from 1940 onwards, published a large number of patents describing the operating conditions and equipment needed for polishing articles made of stainless steels, carbon steels, copper and its alloys, and aluminium and light alloys. The applications were entirely decorative, and electrolytic operation was found to possess technical and economic advantages over ordinary mechanical processes, particularly in the case of stainless steels. The post-war period has seen the development of electrolytic polishing from these tentative beginnings to the full industrial scale, not only in Europe and America, but also in the Soviet Union, Australia, and Japan.

At the time of the discovery of electrolytic polishing, the chemical brightening of copper was already known.[19] In the following years, baths were proposed for brightening and passivating cathodic deposits

of zinc and cadmium, but it was only about 1948 that processes were developed that could really be termed chemical polishing;[20] these are now available for most metals (aluminium, beryllium, copper, carbon steels, germanium, lead, magnesium, nickel, tantalum, titanium, zinc, zirconium) and for many alloys. However, on both the scientific and the industrial scale, chemical polishing is less generally employed than is electrolytic.

To complete this historical account, a brief survey will be given of present trends in electrolytic polishing. It is applied to the following metals and metalloids: aluminium, antimony, silver, bismuth, cadmium, chromium, cobalt, copper, tin, iron (including carbon steels, stainless steels, alloy steels, ferro-silicon, cast iron), beryllium, germanium, gold, hafnium, indium, lead, magnesium, manganese, molybdenum, nickel, niobium, palladium, platinum, tantalum, thorium, titanium, tungsten, uranium, vanadium, zinc, and zirconium. To this list should be added a very large number of single- and multi-phase alloys, some metallic oxides,[21] and graphite.[22]

Micrography forms the largest field of application of electrolytic polishing. Automatic apparatus has been developed commercially[23] (one example of which is shown in Fig. 10 (*a*), Plate XVI), and is finding increasing application for the ultra-rapid preparation (< 1 min.) of specimens for examination under the optical and electron microscopes, and by X-ray and electron diffraction.

The spectacular progress that has taken place in certain branches of metal physics has been largely due to the use of electrolytic and chemical polishing. It will be sufficient to mention in this connection research on the mechanism of plastic deformation, polygonization, and recrystallization, and on the experimental verification of modern theories on dislocations and magnetic domains. Electrolytic polishing has also contributed in no small measure to the success of methods of microhardness determination, of phase-contrast and interferometric methods of examination, and of electron optics, which are being increasingly used by metallographers. As Cottrell[24] has remarked, there is no doubt that the revival in popularity of the microscope in the science of metals is due, in very large part, to the discovery of electrolytic polishing.

There has been a great expansion of industrial applications in Europe, in Japan,[25] and doubtless also in Russia. Many of these applications depend on the special properties of electrolytically polished surfaces, such as resistance to corrosion and wear, frictional properties, reflecting power, and as a good basis for metallic coatings. It is for these reasons that the electrical, electronic and above all the engineering industries use electrolytic polishing for finishing many kinds of component, sometimes of great size. For instance, one of the two electric

locomotives which have achieved a rail-speed record in France contains some electrolytically machined and polished gears[26] (Fig. 11, Plate XVII and Fig. 15, Plate XX).

The electrolytic method is equally applicable in the fabrication of metallic products. A curious feature of electrolytic polishing is that it increases the capacity for plastic deformation[27] to such an extent as to give appreciable ductility to some materials that are normally brittle[28].

Purely decorative applications, which were originally the only ones envisaged, still encounter difficulties in the quality, often inferior, of the semi-finished products supplied by industry. Means must therefore be sought to improve the manufacture of sheet, tubes, bars, sections, &c. Interesting advances have already been made in the case of light alloys[29] and will probably soon follow in certain kinds of steel.

II.—Principles

The anodic solution of a metal under polishing conditions is accompanied by electrical and chemical phenomena. Some of these are readily observed with simple equipment, and throw sufficient general light on the mechanism to warrant serious consideration as bases for all theories on the polishing process.

1. *Electrical Phenomena*

The fundamental experiment by which the author was able to polish copper in orthophosphoric acid[11, 50] is applicable to most metals and to a variety of electrolytes. It consisted in plotting current intensity against the voltage across the terminals of a cell of which the metal to be polished formed the anode. In the first instance, this curve was obtained by reading measuring instruments—voltmeter and ammeter—during a gradual decrease of a potentiometric resistance arm in parallel with the cell. In 1943, the use of the much more informative cathode-ray oscillograph was suggested[30] and this was later successfully taken up by Epelboin and his colleagues.[31]

The curve $I = f(V)$, which is typical of the phenomenon of polishing, is shown at (1) in Fig. 1; curve (2), included for comparison, was obtained with an insoluble, platinum anode. Curve (1) consists of four well-defined parts, of which one, *cd*, which is practically horizontal, corresponds to a constant value of current I over a more or less extended range of values of voltage, V. This plateau is preceded by a region of unstable electrical characteristics (*bc*) and is followed by a rapidly ascending branch of the curve (*de*). In the case of copper in a solution

containing 500–1000 g./l. H_3PO_4, it was found that polishing began at the point *c* and continued along the whole length *cde*. There must therefore be a relationship between the polishing effect and the electrolytic process which is associated with the decrease in current which occurs at a certain voltage. Provided that the area of the cathode is large compared with that of the anode, the cathode reaction—liberation of hydrogen—does not interfere with the form of the curve. It follows therefore that anodic phenomena alone are responsible for the unusual shape of the curve $I = f(V)$.

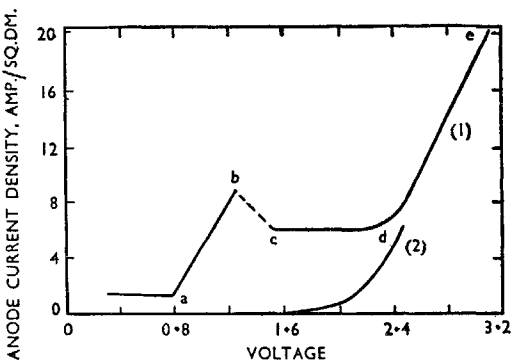


FIG. 1.—Relationship between Current Density and Voltage across Terminals of a Cell Containing an Aqueous Solution of Orthophosphoric Acid (530 g./l.). Curve (1) copper anode and cathode; curve (2) copper cathode, platinum anode.

Capdecomme and Orliac[32] have further shown that in the case of zinc in KOH solution (Vernon and Stroud's method[33] for polishing zinc) the curve $I = f$ (anodic potential) is parallel to the curve $I = f$ (voltage across terminals), as is shown by a simple translation towards the origin O. This was confirmed later for the case of copper in orthophosphoric acid.[34] The determination of the anode potential is clearly of fundamental importance in interpreting these phenomena, but in practice it is easier to measure the voltage across the terminals.

The type of curve shown in Fig. 1 has been found also in the case of other metals capable of being polished in highly conducting electrolytes at low currents and voltages; for instance, cadmium in potassium cyanide,[35] and tungsten in soda solution.[36] With electrolytes of low conductivity, chiefly those of the type consisting of perchloric acid with acetic acid or acetic anhydride, it was at first believed—and some authors still believe[37]—that the $I = f(V)$ curve is almost a straight line inclined to the voltage axis, with a singular point marking a slight change

of direction. In fact, however, aceto-perchloric baths for polishing aluminium[38] and iron[31] give a curve with a well-marked horizontal stage, though to obtain this result it is essential to use a very small anode,[39] and it appears to be equally important to take the following precautions: (i) the rheostat must be in parallel with the potentiometer and not in series,[38, 40], (ii) the voltage must be raised at a certain critical speed[41] and (iii) diffusion around the anode must be reduced, and particularly at the interface (see Fig. 2).

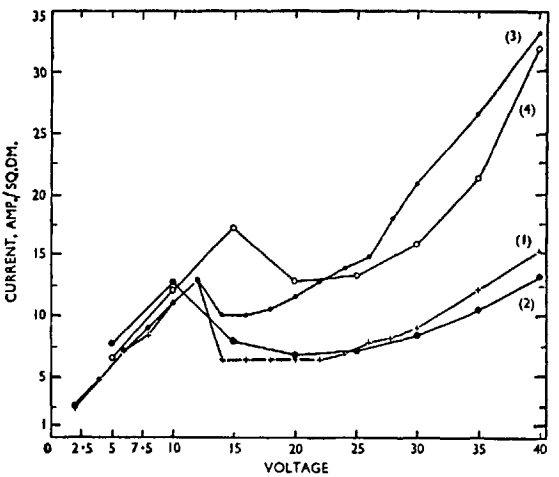


FIG. 2.—Curve showing the Relationship $I = f(V)$ for the Polishing of a 0·34% Carbon Steel in an Electrolyte containing 1000 c.c. Acetic Acid and 50 c.c. Perchloric Acid ($d = 1·60$) showing the effect of shielding the surface at the level of the electrolyte and of the rate of increasing the voltage. The best-defined current plateau is obtained with shielding and with a voltage increase in steps of 2 V. (Curve 1).

KEY

Curve 1 = Area 0·75 cm.² shielded as completely as possible. Voltage increase: steps of 2 V.
Curve 2 = Area 0·75 cm.² shielded as completely as possible. Voltage increase: steps of 5 V.
Curve 3 = Area 0·75 cm.² without shielding. Voltage increase: steps of 2 V.
Curve 4 = Area 0·75 cm.² without shielding. Voltage increase: steps of 5 V.

(*After P. Jacquet*)

The decrease in current at the point *b* (Fig. 1) and its constant value along *cd* indicate an increase in the resistance of the cell which accompanies, as will be shown later, chemical phenomena occurring around

the anode. This explains the marked effect of factors associated with the electrical circuit, the cell geometry, and the diffusion in the anodic layer. The potential measured at the anode is, however, independent of these factors. Honeycombe and Hughan[34] have shown that if the area of a copper anode in a phosphoric acid electrolyte is increased until it is equal to that of the cathode, the horizontal portion of the $I = f$ (voltage at terminals) curve becomes less and less clearly defined, while still persisting on the $I = f$ (anodic potential) curve. It must also be mentioned that the form of the curve $I = f$ (voltage at terminals) sometimes depends on the state of the surface of the anodic specimen. With iron and carbon steel in a perchloric–acetic electrolyte, the current maximum at the point *b* is much lower if the surface is rough (abraded) than if it is polished either mechanically or electrolytically.[42] This must be associated with the formation of a solid film which does not appear after a preliminary polish (see below).

2. *Chemical Phenomena*

These phenomena are associated with changes of a chemical nature occurring at the metal/electrolyte interface. In a large number of cases of polishing, it is possible to see that: (1) at the start of the $I = f(V)$ curve, the rough anode becomes covered with a thin, solid film; (2) under polishing conditions the anode is surrounded by a layer of dense and viscous electrolyte; (3) above a certain voltage oxygen is liberated at the anode, the evolution becoming increasingly vigorous, the higher the voltage and the current.

It is convenient to discuss first the phenomena associated with the anodic layer, which is clearly visible when the electrolyte is colourless and the products of solution are highly coloured (copper and chromium in orthophosphoric acid or iron in a new perchloric–acetic acid mixture). With copper in orthophosphoric acid, microscopic examination shows that the outer limit of the anolyte layer, which is strongly coloured blue, is plane; in other words it is independent of the roughness of the surface of the specimen. It is also apparent that this layer forms from the point *b* onwards (see Fig. 1) and reaches a constant maximum thickness of about 5×10^{-3} cm. along the plateau *cd*.[11] From this it can be concluded that the increase in resistance of the cell between the points *b* and *d* is associated with the layer of electrolyte rich in dissolved metal, and that this layer plays a part in the mechanism of polishing.

Many authors have attempted to determine the composition and properties of this layer surrounding the anode. For instance, Halfawy[43] has found that, for copper in phosphoric acid, the layer contains 100 g. ions of metal/l. and has the properties listed in Table I.

TABLE I.—*Properties of Anodic Layer of Electrolyte (Copper in Phosphoric Acid) (Halfawy*[43])

	Electrolyte	Anodic Layer
Sp.gr. at 25° C.	1·512	1·600
Copper content, g.ions/l.	—	100·5
Coefficient of viscosity (water = 1)	13·8	27·2
Specific conductance, mho	0·145	0·087

The salt obtained by crystallization from the anode layer has been identified by means of its electron-diffraction pattern as $4CuO.P_2O_5.H_2O$. A possible criticism is that this formula does not necessarily represent the compound in solution. Laforgue-Kantzer[44] has shown, by infra-red spectrography of the layer itself, the occurrence of free and combined hydroxyl ions, and suggests, on the basis of chemical and acidimetric analyses, that the dissolved salt is of the type $PO_4(OH)CuH_2$.

The most curious feature recorded in Table I is the appreciable effect of the copper ions on the viscosity of the phosphoric acid solution, although they have only a small effect on the density. There is also a considerable decrease in the conductivity.

Similar results have been obtained by Dale[45] with two industrial polishing electrolytes used for 18:8 stainless steel. His data, recorded in Table II, again show the remarkable increase in viscosity.

TABLE II.—*Properties of Two Electrolytes Used for Stainless Steel (Dale*[45])

	Bath			
	H_3PO_4–Glycerine–Water		H_3PO_4–H_2SO_4–Water	
	Anodic Layer	Electrolyte	Anodic Layer	Electrolyte
Composition: Fe, %	1·0	0·6	3·4	0·5
Ni, %	0·13	0·04	0·5	0·12
Cr, %	0·30	0·13	1·0	0·7
Viscosity, centistokes	248	82	36	9
Resistivity, ohm/cm.	22 (at 82° C.)	15 (at 82° C.)	9 (at 43° C.)	19 (at 43° C.)

The viscous anode layer has been studied much less thoroughly in aceto-perchloric electrolytes. In collaboration with Rocquet,[46] the present author advanced the hypothesis that iron is dissolved in the form of a complex: $[Fe_3(CH_3CO_2)_6(OH)_2]\ ClO_4.\ 4H_2O$.

Plateau and his collaborators[41] found that the anolyte collected during the polishing of aluminium contained a white precipitate consisting of a mixture of chloride, chlorate, and perchlorate of aluminium, soluble in water, which attacked the metal with strong evolution of gas at temperatures above 100° C. Brouillet[47] confirmed the presence of chlorine ions in the anodic layer, and this result is interesting because it undoubtedly has a bearing on the fact that the anodic dissolution of aluminium occurs preponderantly in the monovalent form.[48]

The formation, at the start of electrolytic polishing, of a relatively thick solid film has been confirmed with a large number of metals and many types of electrolyte. In general, this film appears most readily on a surface which has been prepared by abrasion. It has been suggested that it represents the oxide formed naturally in air, but it seems to be more probable that it results from an anodic reaction preceding the formation of the viscous anolyte layer. Very often the solid material disappears spontaneously, falling simply under gravity if the anode is vertical. In the case of iron, it has been noted that the surface then appears much less rough, in spite of the short duration of this stage of electrolysis (40–50 sec.).

The evolution of gas from the anode occurs when the voltage and current density exceed the critical values corresponding to the end of the plateau on the curve (Fig. 1). It is associated with a new anodic reaction—the discharge of hydroxyl ions.

To summarize: the chemistry of anodic dissolution during polishing appears to be complex. It is also difficult to study, because it is always possible that the compounds found by analysis are not necessarily those which are formed initially. Any interpretation of the mechanism of polishing must take into account the presence of the anolyte layer of very high viscosity, which often, though not always, has a lower conductivity than the bulk of the electrolyte, and contains the metal in supersaturated solution, probably in the form of large complex ions.

3. *State of the Anode Surface*

It will readily be appreciated that the electrical and chemical phenomena described above determine the state of the surface of the anode. Observation of this surface whilst the curve $I = f(V)$ is being taken shows that etching takes place along the branch *ab* (Fig. 1), that polishing begins at the point *c*, and that, on passing from one of these parts of the curve to the other, etching is replaced by polishing, or vice versa as the case may be. This phenomenon is used in metallography to polish metallic sections and to develop their structure.

Direct visual observation is not sufficient to enable a correlation to

be made between small changes in surface characteristics and electrolytic factors; for this purpose, it is necessary to examine under the microscope specimens treated for a sufficient time under the electrical conditions corresponding to the different parts of the $I = f(V)$ curve. For example, copper is best polished along the plateau *cd*, and particularly in the neighbourhood of the point *d*. This applies to polishing at low current density. When oxygen is liberated—beginning at the point *d*—the bubbles adhere to the surface and produce relief effects; the metal is still brilliant though rough. The liberation of gas becomes increasingly vigorous along the branch of the curve *de*, and a good polish can be obtained at high current densities, preferably with agitation of the anode[10] and with not too concentrated a solution.

Many metals, in various types of electrolyte, behave similarly to copper in orthophosphoric acid, that is to say, provided that parasitic reactions do not occur, the best polish at low current density is obtained along the horizontal portion of the $I = f(V)$ curve, and in general, it is under these conditions that most small laboratory specimens are polished. But for large components in industrial work, it is more practicable to work in the region of high current densities. Most modern equipment for the automatic polishing of metallographic specimens also works in this region. In this case, the operating conditions (special composition of the electrolyte and its rapid circulation) prevent the disturbing effects of gas evolution, and of overheating, which are not easy to avoid in an ordinary electrolytic cell.

III.—Mechanism of Electropolishing

The lack of fundamental data on the phenomena occurring during the anodic dissolution of metals explains why no complete theory of electrolytic polishing has as yet been formulated, in spite of the large amount of original research work. It is, of course, possible that several mechanisms are involved, or, to be more precise, that the various factors responsible for polishing take on varying degrees of importance, depending on the metal and the electrolyte in use.

As our knowledge of the process increases, it becomes increasingly evident that the phenomenon of anodic polishing is much more general than was at first thought to be the case. This has been confirmed by the discovery of chemical polishing, which has shown that the production of a smooth and brilliant surface is only one particular form of the attack on a metal by a solution which is, in general, very reactive.

When polishing is carried out by mechanical means, the perfectly smooth and brilliant finish is the final result of a series of abrasive operations which progressively remove surface irregularities. Smoothness on the microscopic scale is thus not to be distinguished from that

on the macroscopic scale. Chemical and electrolytic polishing are, however, very different, in that they can give brilliancy to a surface which is still very rough, and this is the characteristic feature of chemical or electrolytic attack under conditions giving rise to polishing.

From the moment that micropolish becomes detectable, the surface attains, more or less rapidly, a macropolish. In other words, micropolishing precedes macropolishing, the smallest irregularities disappearing first. Moreover, the attainment of polish implies that the solution of a metal is a function only of the geometry of its profile, and not of its microstructure. This is not strictly true, however, because any chemical heterogeneity becomes visible as a relief effect, though this effect can be reduced to a minimum if the operating conditions are chosen correctly. In addition it is to be noted that heterogeneities such as Cu_2O in copper, β phase in brass, or $CuAl_2$ in aluminium–copper alloys themselves become polished, on both the microscopic and macroscopic scales, at the same time as the matrix.

Various suggestions will now be reviewed which have been put forward to explain two experimental observations: (*a*) the selective solution of all the asperities forming the macro- and micro-profile, whatever the degree of chemical heterogeneity of the material, and (*b*) the absence of etching on the microscopic scale in chemically homogeneous materials, such as pure metals or single-phase alloys. In general, all theories of electrolytic polishing take into account the anolyte layer rich in solution products. Those of chemical polishing also take a number of special factors into consideration.

1. *The Effect of Resistance*

The first theory put forward by the present author[11] assigned a fundamental importance to the ohmic resistance of the liquid layer formed at a polished copper anode in a phosphoric acid electrolyte. Hickling and Higgins[49] have shown, by means of a composite anode, that the current density over an elevation of 0·15 mm. may be about 2·5 times that over a depression. This could well account for macropolishing, but certainly not for micropolishing.

2. *The Part Played by Diffusion*

It has long been known that all factors which tend to destroy the stability of the anolyte layer by dispersing the products of solution, result in etching of the anode surface. Micropolishing will, however, start again if, under new conditions (higher temperature, agitation, moving the anode from the horizontal to the vertical position), the current density is again brought to its maximum value on the plateau

of the curve.[11, 50] This fact, led Elmore[15] to assign primary importance to diffusion. He assumed that: (1) the ions of the metal are dispersed from the anode by diffusion and convection rather than by electrolytic migration, and (2) the anolyte layer is saturated with the products of solution. Since the rate of solution at any point on the surface is determined by the concentration gradient alone, it is clear that any asperities will be dissolved first. Although the rate of diffusion decreases as the viscosity increases, Elmore derived a theoretical formula which does not take account of this fact, and which, moreover, does not hold in all cases.[51] Viscosity effects do explain, however: (i) why many polishing baths are viscous liquids; (ii) why, for any given bath, increasing the viscosity confers or improves the capacity for polishing[52] (copper is not polished in a sulphuric acid electrolyte, but becomes polished if glycerol is added[53]); and (iii) why the process of dilution and the raising of the temperature hinder the polishing of copper in orthophosphoric acid.[34]

3. *Acceptor Theory*

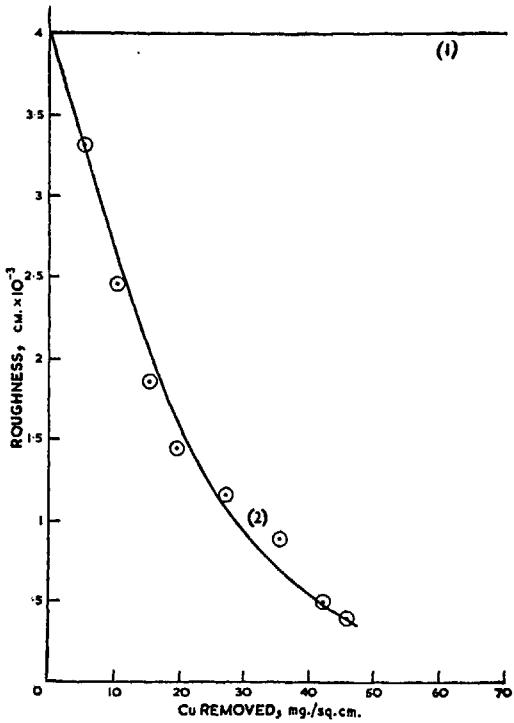
In 1951 Halfawy put forward a theory of polishing different from that of Elmore; he suggested that it was not so much the diffusion of metallic ions that controlled the dissolution of the metal, but the distribution of the anions over the asperities and depressions on the anode, under the action of the electric field and the viscosity.[43, 54] Edwards has considerably developed this new conception.[51] He demonstrated experimentally the important part played by viscosity and suggested that the polishing effect was due to the impoverishment of the anolyte in respect of "acceptors", i.e. anions or certain molecules (for example water molecules, the effect of which had been discussed by Darmois and his collaborators[55]).

Using an extremely elegant technique, Edwards showed that the change in the macroprofile of copper during polishing in phosphoric acid is closely comparable with that deduced theoretically on the basis of the primary distribution of the current, the dissolution being controlled entirely by diffusion.[56] The agreement is excellent when diffusion is reduced to a minimum (shielded anode, high viscosity), but is not so good when convection (unshielded anode, stirring) aids diffusion (Figs. 3 and 4). Incidentally, the effect of stirring had previously been noticed in the case of steel polished in the Jacquet–Rocquet acetoperchloric electrolyte; scratches disappeared in 8 min. when stirring was at the rate of 150 r.p.m., but in 25 min. when it was 900 r.p.m.[57]

Fig. 5 shows that the smoothing effects obtained in a chemical polishing bath—even a simple brightening solution—are not very far from the calculated values. Edwards therefore believes that the

mechanism which he proposed for electrolytic polishing holds in these conditions also, the "acceptors" in this case being "electron acceptors".

Wagner[58] has recently published a mathematical analysis of an ideal electropolishing process, based on a mechanism of diffusion of the acceptors, and the development of the macroprofile deduced from his formulæ agrees very well with Edwards' observations. These formulæ also lead to the conclusion that the smallest asperities disappear first, which again is in accordance with experience.



[*Courtesy Institute of Metal Finishing*

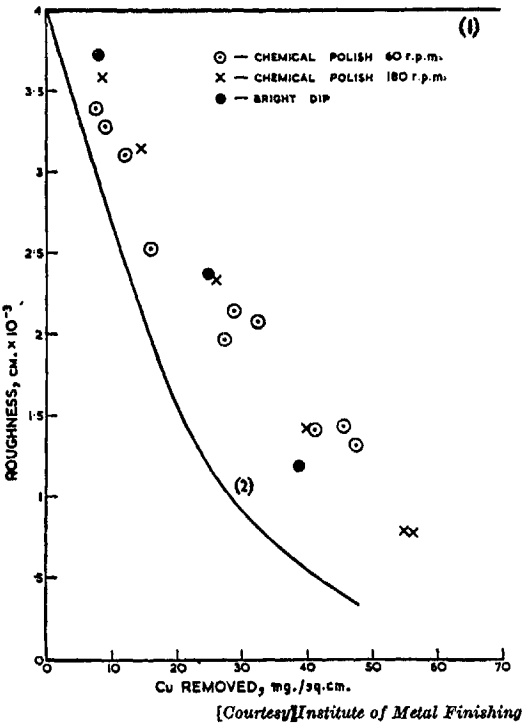
FIG. 3.—Comparison of Theoretical Smoothing Efficiency (Curve 2) with the Experimental Points in Electropolishing of Copper, with Shielded Anode. (*After J. Edwards*[58].)

4. *Passivation Theory*

After the discovery of electrolytic polishing, U. R. Evans put forward an explanation based on the passivation of the depressions in the anode surface,[59] but this is incompatible with the fact that these regions are also subject to dissolution, and that a rough surface may soon acquire a

high degree of brilliance; micropolishing in fact precedes macropolishing.

Nowadays many investigators believe that electrolytic and chemical polishes are, like passivation, connected with the formation of a solid film consisting of products of solution or, more frequently, of an oxide. Numerous facts show a connection between the oxidation of a readily

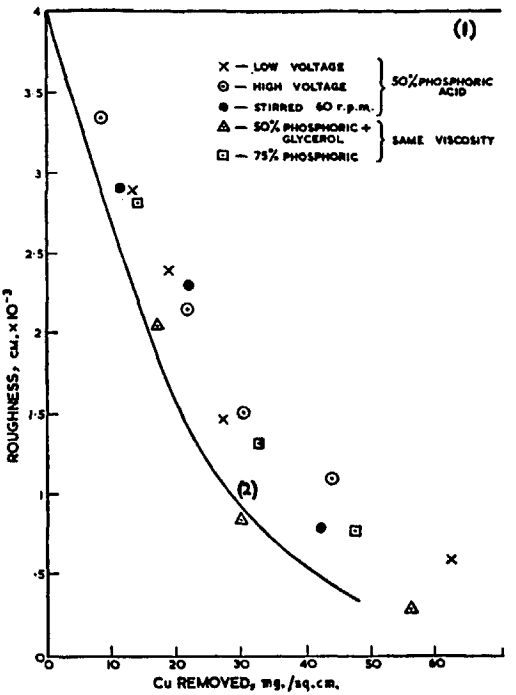


[*Courtesy Institute of Metal Finishing*

FIG. 4.—Comparison of Theoretical Smoothing Efficiency (Curve 2) with the Experimental Points in Chemical Polishing and Bright-Dip Solution. (*After J. Edwards*[56].)

oxidizable metal, such as aluminium or zinc, and its electrolytic polishing. For instance, aluminium can be polished by placing it alternately in an anodic oxidation bath and in one capable of dissolving the alumina film.[60] In the same electrolyte containing phosphoric acid with other additions, it is possible to find conditions of temperature and current density which will give either oxidation or polishing.[61] Tegart and Vines[53] succeeded in polishing iron in sulphuric acid at 60°–70° C. under an e.m.f. of 4·5 V.; the anodic processes involved alternate passivation and activation.

Evidence has recently been published, based on the phenomenon of luminescence, of the existence of an oxide film on zinc during polishing in NaOH solution.[62] Hoar and Farthing have also shown indirectly (by the absence of wetting in mercury) that a compact solid oxide film



[*Courtesy Institute of Metal Finishing*

FIG. 5.—Comparison of Theoretical Smoothing Efficiency (Curve 2) with the Experimental Points in Electropolishing of Copper, with Unshielded Anode. (*After J. Edwards*[56].)

forms on copper during polishing in phosphoric acid,[63] but this conclusion has been questioned by Rowland.[64]

The periodic oscillations in current and voltage that occur before polishing conditions are established have been attributed to alterations of passivation and activation.[65] This explanation is certainly valid in the case of silver in a cyanide bath, because the repeated formation and solution of a solid film—of cyanide or oxide of silver—are clearly observed.[66]

The chemical polishing technique for steel developed by Marshall affords evidence of periodic fluctuations of solution potential (between

0 and 0·5 V.), which agree well, from determinations of loss of weight, with alterations of passivation and activation.[67]

If oxidation is a phenomenon associated with anodic polishing, a film of oxide should be present on the polished surface, and in fact, it is not unusual for such a film to be detected by sensitive techniques, such as electron diffraction or electrochemical reduction by the Miley–Evans method. At the same time, it must be remembered that if the metal is readily oxidized, such a film may well be produced during operations that follow the removal of the specimen from the solution, but cases are known in which the film is so thick (several dozen Ångströms) that it could have resulted only from anodic oxidation. This is so, for instance, in the case of aluminium polished in various baths, such as phosphoric–chromic acid,[68] phosphoric acid–alcohol–glycerol,[69] perchloric acid–alcohol,[68] and fluoboric acid.[70] On the other hand, aluminium, polished in the Jacquet aceto-perchloric bath, gives an electron-diffraction pattern identical with that of the pure metal,[68] and the same applies to copper polished in phosphoric acid, provided that certain precautions are taken while handling the specimen.[71] This subject will be discussed later in considering important facts connected with the chemical nature of the polished surfaces. Finally, mention should be made of the fact that mild steel, chemically polished in a mixture of oxalic acid and hydrogen peroxide, is covered with an oxide film approximately 45 Å. in thickness.[72]

These experimental facts, taken together, tend to confirm that electrolytic and chemical polishing are concerned with the alternate formation and dissolution of a solid film, in other words, with successive processes of passivation and oxidation. Depending on the respective speeds of these two processes, the thickness of the passivating film will be greater or less.[73] As has been mentioned, it is possible to change over from more or less complete passivation to polishing by altering the operating conditions, such as temperature and current density, and it is also possible to make some slight alteration in the composition of the electrolyte.[49]

Without exception, under the usual optimum conditions of electrolytic polishing, the oxide film either cannot be detected (i.e. its maximum thickness is 10 Å.) or has a thickness limited to a few dozen Ångströms. Even for nickel, for which the sequence of alternations of passivation and activation is particularly well marked,[65] the film remains very thin, because the anodic overvoltage falls to zero only 0·05 sec. after switching on the current, whereas in the case of true passivation the fall of the overvoltage requires a considerable time.[74]

The transitory formation of a solid film—either salt or oxide—can contribute to the macropolishing, because the film is more porous and

more readily soluble on the asperities than elsewhere. Yamaguchi[75] has noted, for example, that sharp asperities become rounded after the formation and removal of a thin oxide film.

The same explanation holds for chemical polishing, but here another mechanism has also been proposed, involving the selective solution of the asperities by the setting up of local voltaic cells between those regions where the film is easily removed and the depressions where the film is more stable.[67]

It should be noted that a theory of polishing involving the transitory formation of a solid film is not inconsistent with Edwards' theory of acceptors. The viscous anodic layer serving as a screen for the arrival of acceptors at the surface is still the fundamental concept. The presence of a thin film of salt crystallizing from such a layer, rich in the products of solution, or the discharge of hydroxyl ions leading to the formation of oxide, are secondary reactions, but they nevertheless play an important part in micropolishing.

5. *Ionic Adsorption Theory*

Darmois and his collaborators have put forward a theory of polishing involving the adsorption, on the anode, of the anions of the electrolyte.[76] This theory was first advanced in connection with electrolytes containing perchloric acid or its salts, but it was afterwards extended to cover polishing at high temperatures in fused-salt mixtures. This theory, and its experimental basis, have been discussed at length in a recent paper,[77] and only a brief review will be given here.

Under polishing conditions, the anode becomes covered with a thin but compact layer of ClO_4^- ions, which are capable of setting up an electrostatic field sufficiently intense to detach the metal ions. The authors draw attention to the similarity between the current plateau on the $I = f(V)$ curve and the discharge barrier in rarefied gases, and this, in their view, eliminates any hypothesis depending on the formation of an oxide film. Goche[78] has in fact succeeded in polishing copper in a discharge tube, but only when the rarefied gas was oxygen. In these experiments, which, it must be emphasized, dealt almost entirely with aceto-perchloric baths, Darmois and his colleagues do not appear to have taken sufficient account of the temperature factor, which can profoundly modify the anodic processes[79] (see p. 184).

6. *Other Theories*

As a matter of interest, mention may be made of the curious theory of Vozdvizhensky,[80] who believed that anodic dissolution depended only on the structure, and not on the geometry, of the anode. Of somewhat

greater importance is the work of Mercadié,[81] who tended to make a distinction between electrolytes of which the constituents were wholly dissociated and those only partially dissociated. The latter alone could constitute polishing baths, because in the former the space charge would tend to equalize the current density at all points on the anode. In passing, it is worth while noting that the acceptor theory is particularly plausible in cases where the solution products from the anode are complex salts which are little dissociated.

Knuth-Winterfeldt[82] believes that the heating which takes place in the course of electrolysis is an important factor in polishing, and considers that the maximum temperature must be reached in the layer adjacent to the anode and not on the metal surface itself.

7. *Micro- and Submicropolishing*

In the present state of knowledge, the acceptor theory and that of partial passivation explain satisfactorily polishing on the macroscopic scale. The true criterion of chemical polishing, and even more of electrolytic polishing, is the absence of the phenomenon of etching, which always occurs on metals when they are exposed to a wide variety of reagents, and occurs even in polishing baths if conditions are not maintained at the optimum. This implies that, under conditions appropriate for polishing, the rate of solution on the microscopic scale is constant. Of course, this applies to a metal or solid solution which is reasonably pure, for different constituents have their own specific rates of attack, although these may be very similar to those of the matrix if the electrolyte and the operating conditions have been suitably selected.

Edwards, Hoar and Mowat, and Darmois and his colleagues have put forward arguments, apparently very convincing, in support of their respective theories of acceptors, dissolution through a solid compact film, and ionic adsorption, all of which explain satisfactorily the phenomena of micropolishing. Each one of the suggested mechanisms leads to the conclusion that the differences in potential energy between the atoms of a phase do not have to be taken into account in determining the removal of one atom in preference to another. In other words, this removal should occur purely by chance, and it follows therefore that the structure on the scale of the atomic lattice takes no part in it.

It is known, however, that, even when polishing under the most favourable conditions, observations made by certain optical means, such as out-of-focus adjustment, phase contrast, or oblique illumination, show up certain details of the microstructure, such as grain boundaries,[83] or slip bands if the material has been heavily cold worked. A method of high sensitivity has enabled these observations to be clarified

and generalized.[84] Fig. 13 (Plate XVIII) shows, at high magnification, the structure, as revealed by electrolytic polishing, of a specimen of brass, as annealed, as cold rolled, and as deformed in tension and in reversed bending after annealing. All the surfaces have been well polished, for there is complete absence of corrosion markings, but it is also quite clear that the rate of attack has been determined by the fine structure of the atomic lattice. It is impossible to say, therefore, that the removal of the atoms has taken place haphazardly. Electron micrographs of super-purity aluminium and of certain of its alloys often show a substructure,[85] indicative of selective attack in relation to the crystal lattice.[86]

It must be emphasized that the details visible in the micrographs (Fig. 13) correspond to minute differences only of surface level, of the order of 20–100 Å. Consequently it is necessary to consider not only macro- and micropolishing, but also a submicropolishing which is extremely sensitive to the conditions of electrolysis. In the case of copper and α-brass, for instance, very small changes in the e.m.f. applied to the cell terminals while operating along the current plateau are sufficient to alter markedly the quality of the submicro-relief. In any theory of electrolytic polishing, this phenomenon must obviously be taken into consideration; in the author's view, it is clearly bound up with the formation of a thin solid film whose characteristics reflect the variations in reactivity of the crystallographic lattice.

8. *Conclusions*

Whatever theory is adopted to explain the phenomena of chemical and electrolytic polishing, from the practical point of view it is important to remember that all degrees of polish are possible, ranging from the perfect surface to the usual more or less etched one resulting from attack after a very good mechanical polish. At the same time, there is a great difference between the "reactivity" of a surface polished mechanically and one polished electrolytically, owing to the disturbed structure of the former. The tendency of a metal to become etched is in fact much reduced by electrolytic polishing (Fig. 14, Plate XIX).

The degrees of difference between the perfect polished surface and the etched one depend on the nature of the metal or alloy, on its metallurgical history, and on the exact operating conditions selected.

Hence it may be said—and this view will appear even more firmly substantiated after a comparison between the characteristics of electrolytically and chemically polished surfaces on the one hand and mechanically polished surfaces on the other—that there is no such thing as an electrolytically polished state or a chemically polished state, but rather is there a wide range of both finishes.

IV.—General Observations on Technique

A distinction should be made between two techniques of electrolytic polishing, one covering small laboratory specimens and the other industrial components. In the first case, it is a question of obtaining optimum surface characteristics, whereas in the second the primary considerations are ease of working and the lowest possible cost.

Historically, the laboratory methods were developed first and are now completely determined for all metals and alloys. A selection of suitable methods is given in Appendix I (pp. 212–233). Industrial processes are less fully developed, and in fact cover only the carbon steels, stainless steels, aluminium and some of its alloys, copper and its alloys such as brass, bronze and nickel silver, nickel, chromium, and some special alloys such as the Nimonics. Information on operating conditions and economic factors are available in the literature.[87]

Although electrolytic polishing is an anodic process, some metals can be polished in special baths with alternating current.[88]

As far as chemical polishing is concerned, published bath compositions apply equally to laboratory specimens and to industrial articles. Information on these is also given in Appendix II (pp. 234–238).

1. *Electrolytic Polishing*

(*a*) *Laboratory Technique*

According to circumstances, experimenters may use either a simple cell and the appropriate electric circuit, or one of the automatic, commercial, pieces of apparatus. Both methods have their advantages and disadvantages, which are summarized in Table III.

It is hardly possible to use the automatic instrument for purposes other than the preparation of metallographic specimens, and the cell technique is generally essential for polishing specimens required for physical, mechanical, or physico-chemical tests. Special equipment has also been described for electro-machining.

(i) *Automatic Apparatus.* Initially designed and constructed in the laboratory,[89] these instruments are now sold commercially. There are several types.[90] The most recent, shown in Fig. 10 (Plate XVI), uses a small number of electrolytes which are well suited for polishing and attacking all metals and alloys, except the noble metals. Auxiliary equipment (Fig. 10 (*b*)) is now available for polishing a small area of a large component, such as a ship's propeller, airscrew, crankshaft, &c.

(ii) *Electrolytic Cell.* As can be seen from the Appendix, many metals and alloys can be polished in baths containing perchloric acid and acetic acid or acetic anhydride. Darmois and his colleagues[91] have established an empirical rule giving the optimum composition for a bath of

this type: it is that which has the maximum resistivity. Perchloric acid may sometimes be replaced by one of its salts, such as magnesium perchlorate.[92] This empirical rule, however, does not always hold.[93]

TABLE III.—*Features of Simple Cells and Automatic Apparatus for Electropolishing*

Simple Cell	Automatic Apparatus
(1) Direct current or rectified alternating current may be used.	(1) Supply must be alternating; a rectifier is incorporated in the apparatus.
(2) Specimens of any shape may be polished completely with surface areas up to 10–15 cm.^{2}	(2) Polishing is limited to an area of 0·2–3·0 cm.^{2}, and to a plane surface only.
(3) Very low current densities (a few amp./dm.^{2}).	(3) High current densities (50–100 amp./dm.^{2}).
(4) Possibility of dissolving very small thicknesses of metal (0·5–1 μ).	(4) Rate of dissolution very great.
(5) Operating conditions must be closely controlled (temperature, stirring, current density, voltage, &c.	(5) Quasi-automatic control of optimum conditions, as laid down by the makers of the instrument.

According to Epelboin,[94] the best polish with aceto-perchloric electrolytes is obtained under electrical conditions corresponding to the maximum internal resistance of the cell (tangent to the $I = f(V)$ curve). Utilizing this concept, several authors have developed circuits which include a Wheatstone bridge, with satisfactory results.[95]

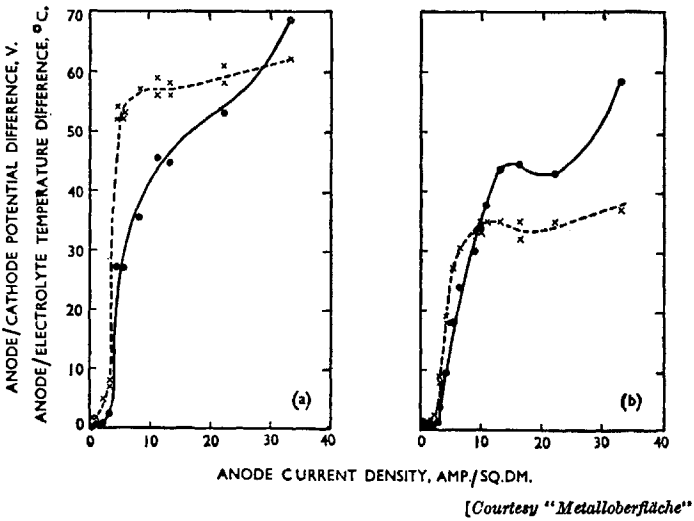
It is important to note that freshly prepared aceto-perchloric baths do not usually give the best polish; they must first be enriched with metal ions, either by anodic dissolution or by the addition of salts.[46, 93]

The Hull cell, well known to electroplaters, has been suggested as a means of finding the optimum polishing conditions for highly conducting electrolytes, such as phosphoric acid, and also of studying the effects of certain additions to such baths.[96]

Agitation is often useful for suppressing waviness of the surface, of which there is always a risk during prolonged electrolysis. It can be effected by rotation of the anode[97] or of the cathode,[98] by moving the anode,[99] or by means of a mechanical stirrer in the solution.

With baths of low conductivity it is nearly always necessary to provide an efficient cooling system. Using the aceto-perchloric bath for polishing iron and steel,[46] Heyes and Fischer[100] found that the formation of the viscous anolyte layer caused a sharp rise of temperature,

which was greater if the baths had previously been used (Fig. 6). This heating is restricted to the anode and reduces the quality of the polish. The rise in temperature of the specimen may also bring about structural changes. This is of especial importance in the case of super-purity aluminium, which recrystallizes at, or a little above, room temperature. In the case of aluminium, the temperature may exceed 70° C., thus explaining the etching effects obtained at high current densities.[93]



[Courtesy "Metalloberfläche"

FIG. 6.—Relationship between the Rise of Temperature of the Anode and the Voltage across the Terminals of the Cell in Electropolishing of Iron in the Jacquet–Rocquet Electrolyte.

(*a*) New electrolyte. (*b*) Used electrolyte.

●———● Temperature difference.

×------× Potential difference. (*After Heyes and Fischer*[100])

For some micrographic work it is necessary to polish specimens above room temperature. In indium–thallium alloys, the phase stable at high temperatures is polished at 100° C. in a nitric acid–hydrochloric acid–carbitol bath. Wojcik has polished steels at 200°–350° C. in a mixture of orthophosphoric acid and ammonium sulphate, whilst metals of the platinum group and graphite are polished in mixtures of fused salts. Details are given in the Appendix.

(iii) *Special Apparatus.*—Apparatus has been described in which the normal cell is not employed. This includes "brush" and "disc" polishing,[101] and the use of liquid jets.[102]

(iv) *Electro-machining.*—It is possible to use electropolishing techniques for reducing the diameter of wires, or the thickness of sheets, for producing fine points without the use of tools, and for making test-pieces for mechanical or dilatometric tests. In all such cases, the surfaces obtained possess a high degree of polish.

For reducing the diameter of wires (down to about 3 μ), or for thinning sheets,[103(a)], and for cutting points,[104] the usual electrolytes are used in special cells. One very interesting application is the preparation of sheets sufficiently thin in places to be used for direct transmission of the beam of electrons from an electron microscope.[103(b)]

For machining test-pieces, rather more complicated apparatus is necessary (Fig. 17, Plate XXI) with extremely high current densities, so that the usual electrolytes cannot always be employed.[105]

(*b*) *Industrial Electrolytic Polishing*

Industrial installations are very similar to those used for chromium plating (Fig. 12, Plate XVII). The baths are made of stainless steel, of iron coated with lead or plastic, or sometimes even of aluminium. The anode bars which carry the component can be slowly moved backwards and forwards. Cathodes, which are of large area, are made of lead or stainless steel. Current is supplied from dry rectifiers with continuous regulation up to 14–16 V. The Hispano Suiza superfinishing technique requires a higher voltage (50–60 V.) supplied by a generator. The electrical energy needed depends on the capacity of the tanks, 1 amp./l. of bath being usually allowed. Baths as large as 15,000 l. and currents up to 90,000 amp. are used.[106]

Industrial electrolytes most commonly used for steels are mixtures in various proportions of sulphuric and phosphoric acid, often with additions of chromic acid.[107] Aluminium and its alloys are polished in baths of similar types,[108] whilst copper and brass require aqueous or alcoholic solutions of orthophosphoric acid, often containing special additions.[109]

Other types of industrial bath are also in use. For instance, the superfinishing process for steel parts developed by Hispano Suiza employs a mixture of orthophosphoric and chromic acids,[110] and this bath can be used for polishing other metals. The oldest process of all for polishing pure aluminium—the Brytal process—uses an alkaline electrolyte.[16]

Industrial baths differ from the majority of laboratory electrolytes in operating at temperatures between 50° and 90° C. One exception, however, is the perchloric acid–acetic anhydride bath used industrially in Germany for carbon and stainless steels (Fig. 16, Plate XX): this has to be cooled.[100, 111]

The control and regeneration of electrolytes is an important matter

in industrial applications of electrolytic polishing, the main factors in this connection being viscosity, density, relative concentration of components, and content of dissolved metal. Except in the case of baths based on phosphoric acid used for polishing copper—which are stable since the metal is deposited on the cathode—regeneration is accomplished by removing a portion of the bath periodically and replacing it by an equal volume of new solution. It is interesting to note that the aceto-perchloric bath still functions satisfactorily at an iron content as high as 100 g./l., whereas in phospho-sulphuric baths more than 10–12 g./l. of iron cannot be tolerated.[112]

The presence of chromic acid introduces a complication, as the chromium is reduced from the hexavalent to the trivalent state during operation. A special method of regeneration has been described for such electrolytes.[113]

2. *Chemical Polishing*

Chemical brightening has long been known for copper, brass, zinc, and cadmium,[19] but during the last few years the process has been considerably improved by the use of new baths and has been extended to other metals.

On the industrial scale chemical polishing is used for aluminium and some of its alloys, and for copper and such alloys as brass and nickel silver. Certain baths, which have a brightening and passivating effect, are sometimes used for electrodeposits of zinc and cadmium.

On the laboratory scale, chemical brightening has also been used for iron, mild steel, lead, nickel, magnesium, germanium, titanium, and zirconium. The compositions and suitable operating conditions are listed in the Appendix, and fuller details can be found in recent publications.[114, 115]

The first patent of the Battelle Memorial Institute[20] describing modern chemical polishing did not mention its application to aluminium, but in a short time many types of bath were developed in different countries for this metal, and a great variety of them now exists. In the Alupol industrial process,[116] aluminium and its alloys are chemically polished in two stages: first in an alkaline bath having great power of smoothing, and secondly in an acid bath which confers a high degree of brilliance. Hérenguel[117] has used the same principle in chemically polishing micrographic specimens, but his two baths were both acid, consisting of mixtures of sulphuric, phosphoric, and nitric acids in different proportions.

Until recently, all chemical polishing baths suffered from three serious defects: (1) faulty operation above a certain concentration of dissolved metal; (2) the need to be heated to 55°–90° C.; and (3) a very

corrosive action on the tanks, stainless steel or glass being the only materials that could be used. Attempts have been made to eliminate these defects by using other bath compositions, less concentrated as regards acids and containing additions. In the case of copper alloys, a more dilute acid bath containing hydrochloric acid and other undisclosed compounds has been found to work satisfactorily at 25°–35° C., and to retain its efficiency even after 300 g. of metal have been dissolved per litre of bath.[118] For light metals, a bath having a low acid content still works well after it has been used for polishing several dm.^{2}/l.[119]

The amount of material removed in the attack varies considerably with the metal, the composition of the bath, and the temperature. For example, in the original Battelle solutions, the speed of dissolution varied between 15 and 75 μ/min.

V.—The Dangers of Electrolytes Containing Perchloric Acid

Ever since 1940 the view has been taken that certain precautions must be observed in handling electrolytes containing perchloric acid in order to avoid gross overheating and contact with organic materials and with bismuth, all of which are likely to cause an explosion.[120] In fact, however, the danger does not arise with dilute solutions, even in alcoholic solution, as used in electrolytes of the de Sy–Haemers type, which contain less than 4% $HClO_4$.[121] Nevertheless such mixtures should not be subjected to prolonged heating, because of the risk of a high concentration.[122]

Metallographers were very disturbed by a publication reporting two accidents, one of them fatal, in German laboratories.[123] The first accident was easily explained as being due to the use of a concentrated solution of perchloric acid (1 part) in *iso*amyl alcohol (2 parts). In addition, contrary to statements made in the publication, witnesses testified that the operator had absolutely no practical experience of electrolytic polishing and that the apparatus itself was very defective, with a danger of short-circuiting. Details are lacking of the second explosion, which occurred with a mixture of 1 part of $HClO_4$ (65%) in 2 parts acetic anhydride.

The uneasiness of metallographers was greatly increased by the extremely serious accident which occurred at Los Angeles in February, 1947, when 800 l. of an aceto-perchloric acid bath exploded, causing 15 deaths, 150 wounded, and damage to the extent of about $2 million.[124] Wide publicity was given to the accident, and, as a result, the use of perchloric acid was strictly forbidden in many laboratories, particularly in Great Britain. Searching enquiries were made into the circumstances of the Los Angeles explosion by government officials and

insurance companies, but unfortunately the results of the enquiry did not reach scientific circles, as is shown by such statements as the following, written in 1951: "No-one knows what caused the tank to explode at the O'Connor Electroplating".[125] It is therefore very important to summarize the conclusions reached in these enquiries, namely:

(1) The so-called inventor of the process was an adventurer without technical knowledge.

(2) The electrolyte contained 75% of perchloric acid ($d = 1{\cdot}72$) in acetic anhydride.

(3) The automatic cooling system was not working, and the temperature of the bath was well above the normal working limit of 27° C.

(4) On the day of the accident, the supports of the specimens had been partially insulated by "Tenite 2" (acetobutyrate of cellulose).

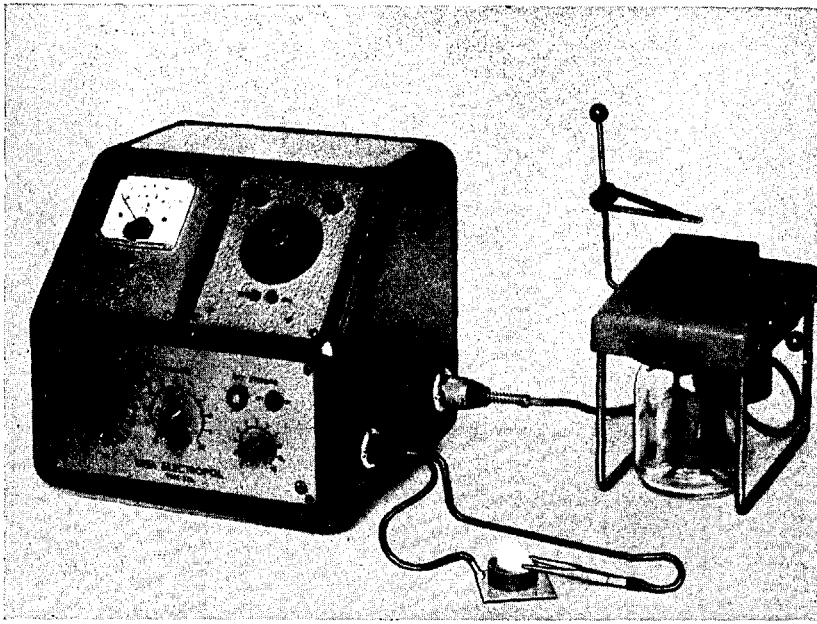
The very high concentration of perchloric acid, the rise in temperature, and the contact with organic matter were undoubtedly the factors responsible for the explosion, and this has been confirmed by a simple experiment carried out by one of those who investigated the original incident.[126]

Médard and Sartorius[127] have made a thorough investigation into the liability of mixtures of perchloric acid and acetic anhydride to be exploded by detonators, heating, sparks, &c. Fig. 7 shows the range of dangerous concentrations. It is clear that the O'Connor bath lies within this range, and that all electrolytic polishing baths, even those containing most perchloric acid, lie well outside it. The point *C* indicates the mixture corresponding to complete combustion (68 vol.-% $HClO_4$ ($d = 1{\cdot}59$) + 32% acetic anhydride) and point *A* indicates the "anhydrous" mixture (24·3% $HClO_4$ + 75·7% acetic anhydride). Mixture *C* detonated with a cap containing 0·6 g. of mercury fulminate, but mixture *A* did not do so, even when the detonator was supplemented with 50 g. of penthrite.

This work showed equally clearly that a spark, or a red-hot wire, would not cause an explosion in a polishing bath. The baths will, however, catch fire if brought to the boiling point and exposed to a flame. If strongly heated, say in a fire, there is a risk that large volumes of these mixtures would lead to an explosion.

This work confirms the harmless nature of aceto-perchloric baths, provided that the operator observes a few simple precautions, chiefly as regards temperature and the absence of any flame, and certainly the replacement of acetic anhydride by acetic acid would reduce the danger still further.

The mixtures must be made by pouring one of the reagents very



[*Courtesy H. Struers Chemiske Laboratorium and Dr. E. Knuth-Winterfeldt*

FIG. 10(*a*).—Disa-Electropol Apparatus for Polishing and Etching Micrographic Specimens up to 3 cm.^{2} in Area.

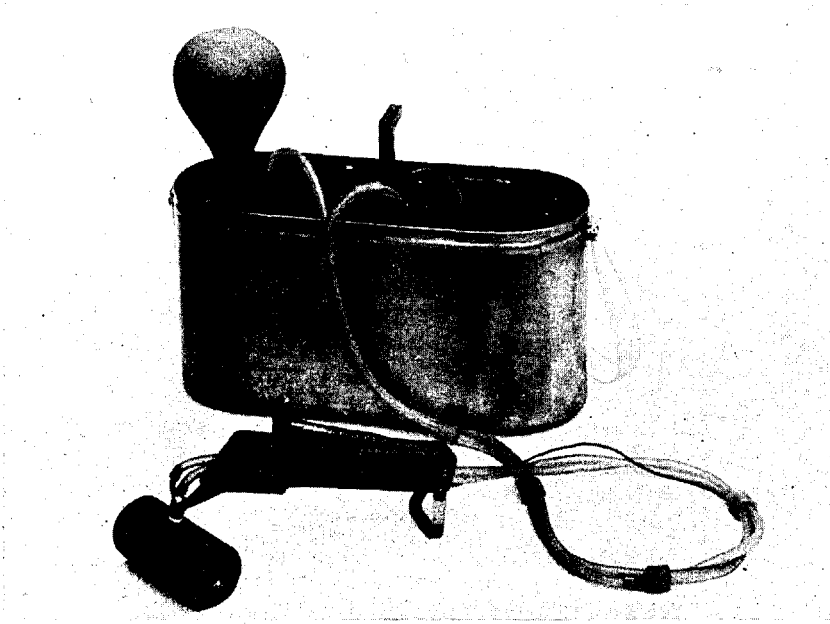
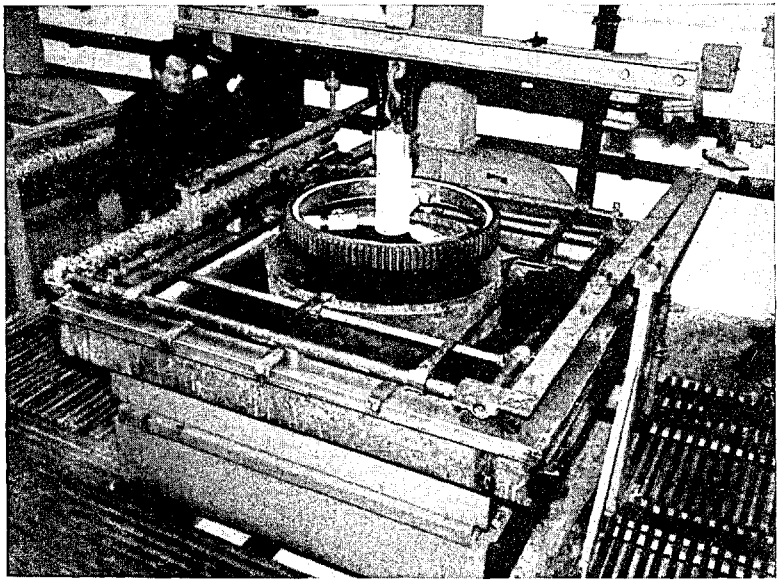
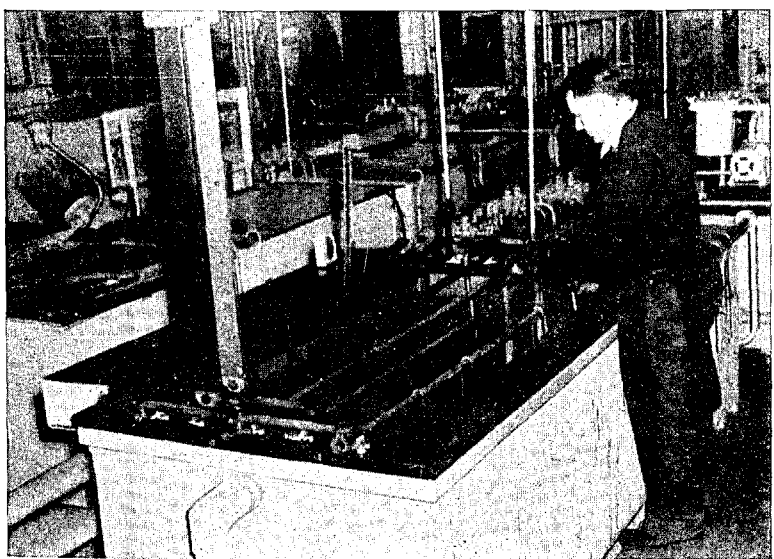


FIG. 10(*b*).—Movipol Auxiliary Apparatus Comprising a Small Portable Cell for Polishing an Area of about 0·5 cm.^{2} on a Specimen or on a Metallic Object of Considerable Area.



[*Courtesy Société L'Engrenage, Saint-Etienne, and Société Jacquet-Hispano-Suiza, Bois-Colombes*

FIG. 11.—Plant for Electromachining and Electropolishing Gears. The gear shown here measures about 1 m. in dia. Gears for the French locomotive BB9004, which gained the rail-speed record of 331 km./hr. in 1955, were polished in this tank.



[*Courtesy Standard Motor Co., Ltd., Coventry, and Modern Electrolytic Patents and Processes, Ltd., London*

FIG. 12.—Close-up of Aluminium Electropolishing Tank, showing the Cathodes in Position and the Anode Bars on which the Operator is Placing a Workpiece.

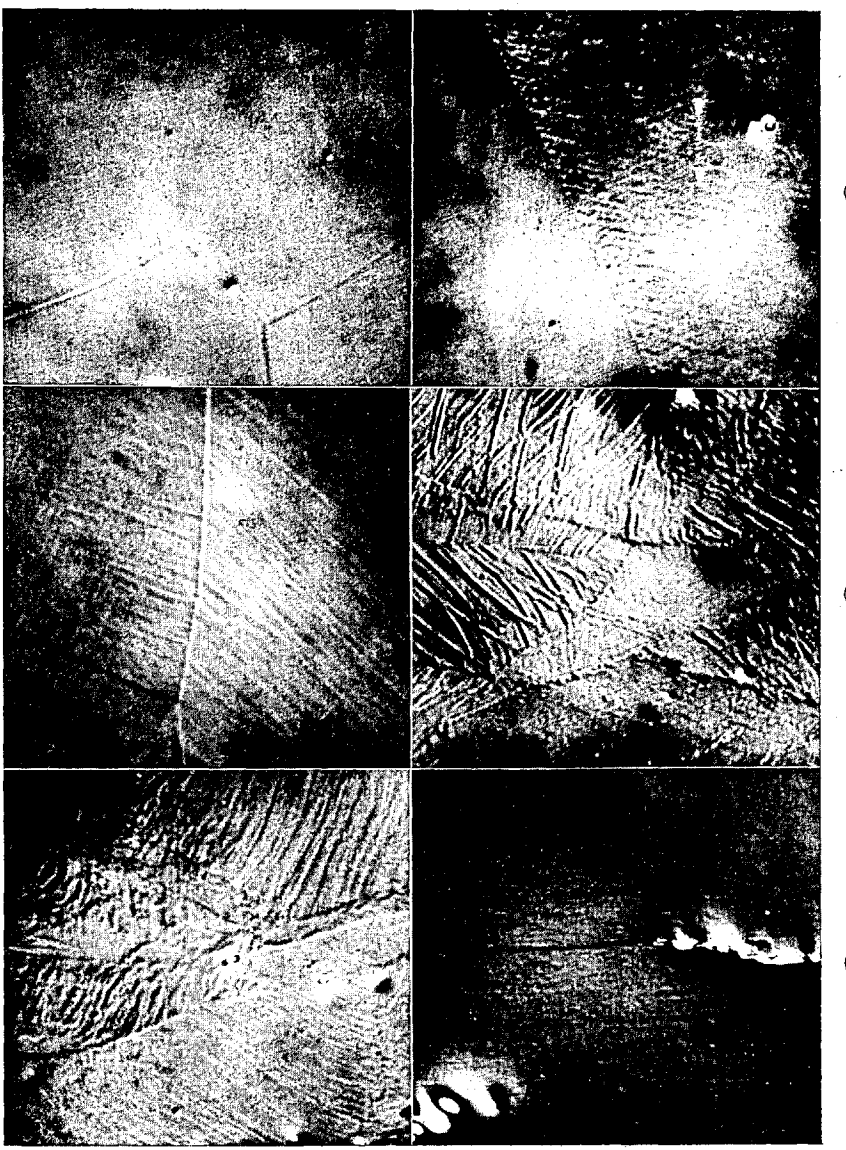


FIG. 13.—α-Brass Containing 67% Copper Polished Electrolytically in Orthophosphoric Acid ($d = 1{\cdot}44$) at 1·75 V. Examination by means of the Nomarski apparatus (interference contrast in polarized light). × 2000.

(*a*) As initially annealed. (*b*) Tension 13·75 kg./mm.^{2} (elongation 6%). (*c*) Tension 18·30 kg./mm.^{2} (elongation 15·6%). (*d*) Extension to point of fracture (35 kg./mm.^{2}). (*e*) Rolled to a reduction in thickness of 70%. (*f*) Failure under alternating stress (266,000 cycles at 13 kg./mm.^{2}). The bright line on the right is the end of a microfatigue crack.

With test-pieces submitted to plastic deformation, electrolytic polishing brings to light a sub-structure of the crystals, involving a mechanism of sub-microetching which is associated with disturbances of the crystallographic lattice. (*After P. Jacquet* [84])

(Reduced by ⅓ in reproduction)

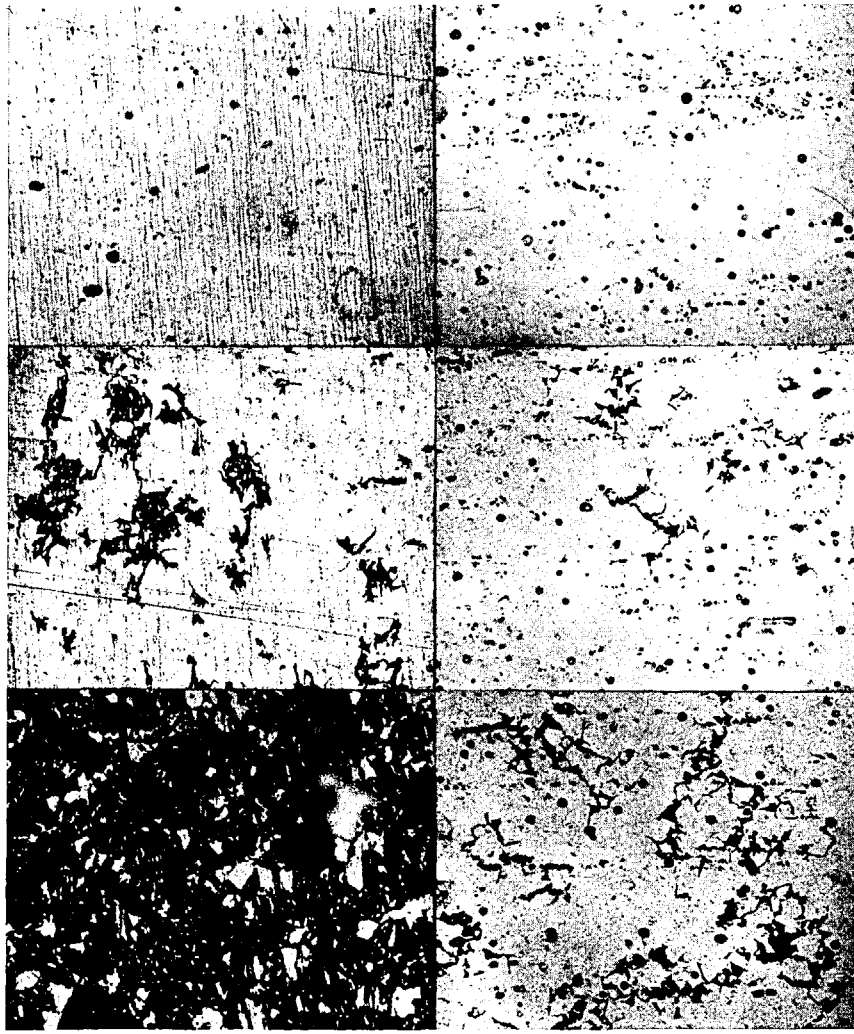
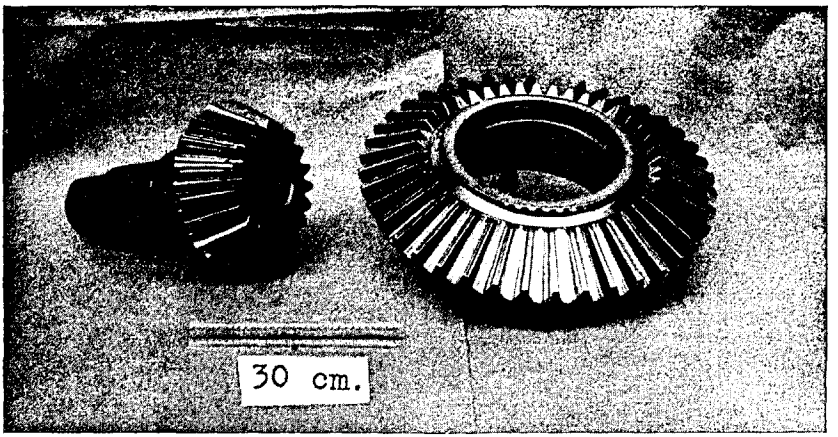


FIG. 14.—Aluminium of 99·5% Purity Rolled and then Annealed for 30 min. at 450° C. × 63. The surface was given a treatment in dilute NaOH solution, electrolytically polished for 10 min., then abraded mechanically on emery papers Nos. 1F, 0, and 000, under paraffin, and finally cleaned by means of benzene and alcohol. Half of the specimen was left in this condition, and the other half was electrolytically polished. The whole surface was then immersed in hydrochloric acid (13 wt.-%).

(*a*) As polished mechanically. (*b*) Same specimen as (*a*), immersed for 7 min. (*c*) Same specimen as (*a*), immersed for 17 min. (*d*) As polished electrolytically. (*e*) Same specimen as (*d*), immersed for 7 min. (*f*) Same specimen as (*d*), immersed for 17 min.

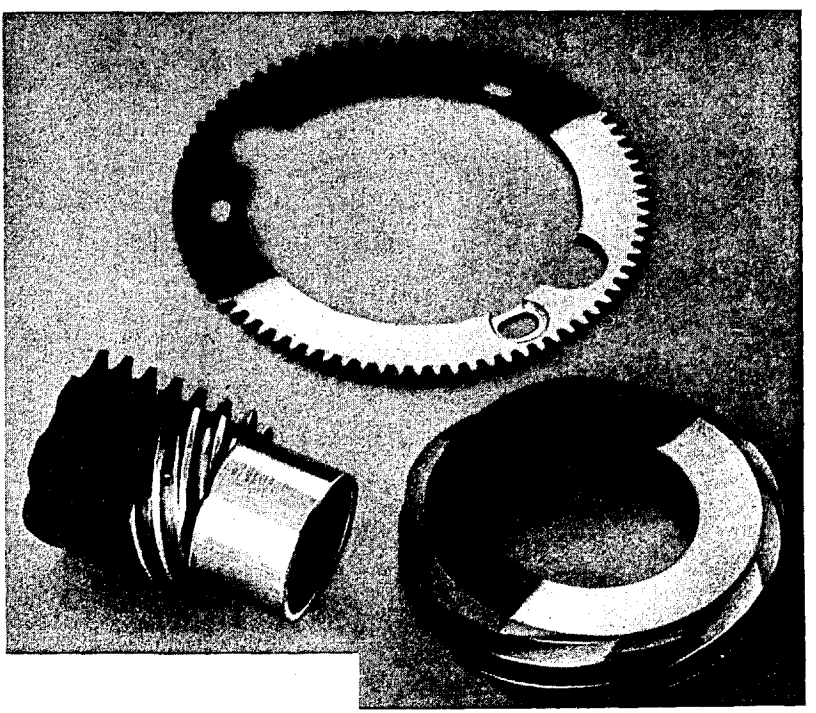
(*After P. Jacquet*[197])

(Reduced by ¼ in reproduction)



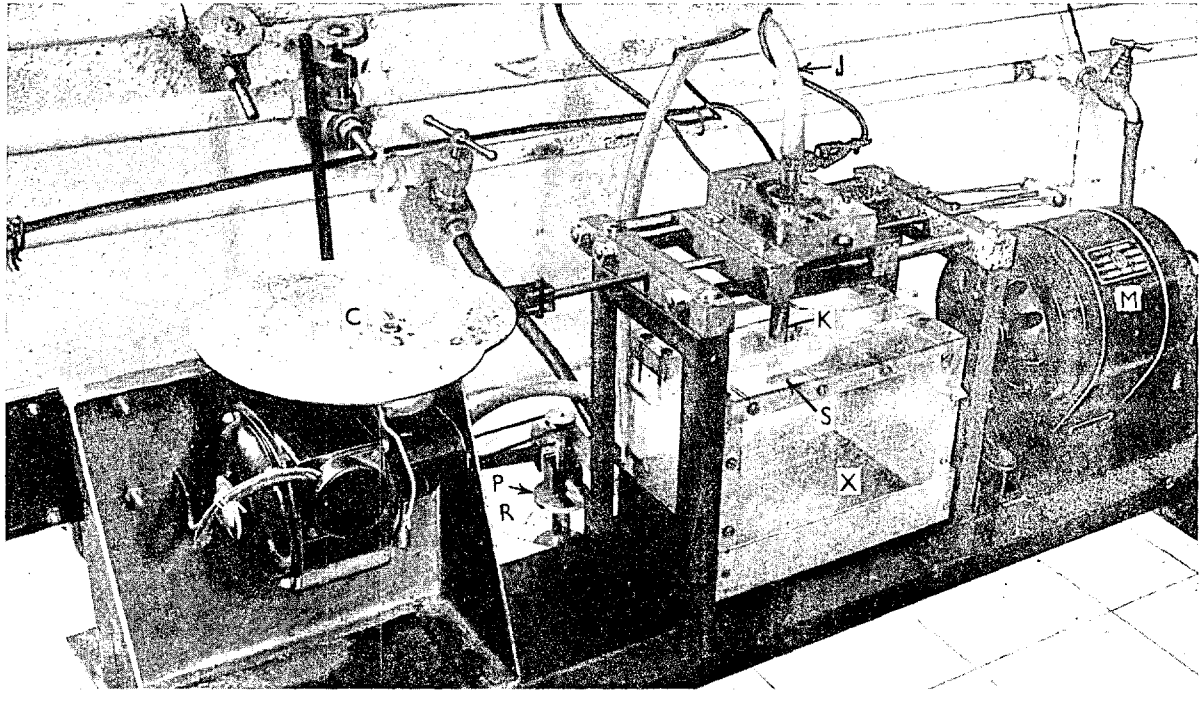
[*Courtesy Société Batignolles-Châtillon and Société Jacquet-Hispano-Suiza*

FIG. 15.—Crown and Pinion of the Transmission Gear of a Diesel Locomotive, Electrolytically Machined and Polished.



[*Courtesy Dr. J. Heyes and Dr. W. Kampschulte and Co., Solingen*

FIG. 16.—Some Examples of Polished Engineering Components. A part of the surface of each has been polished in an industrial plant by means of aceto-perchloric acid electrolyte.



[*Courtesy Commissariat à l'Energie Atomique and MM. Stohr and Englander*

FIG. 17.—Apparatus for Electromachining Metallic Specimens.

KEY

J = Supply of electrolyte to cathode.
C = Cam for horizontal displacement of cathode.
K = Cathode.
X = Plexiglass cell, hermetically sealed.
S = Specimen, mounted on axis of motor M.
R = Electrolyte reservoir.
P = Pump for circulating electrolyte.

PLATE XXI

(*a*) (*b*)

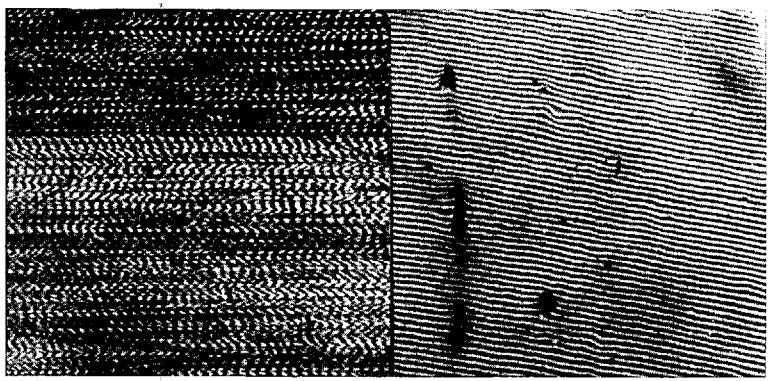
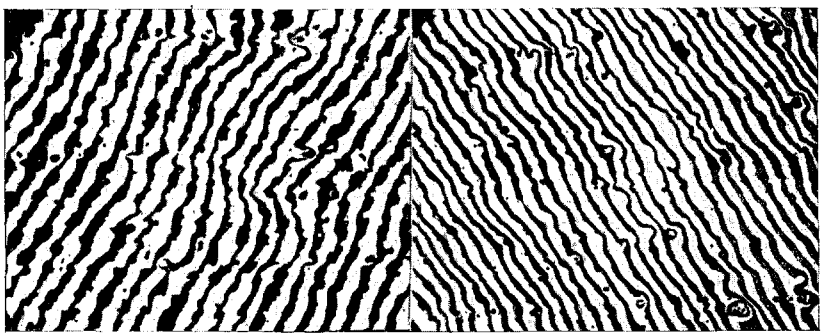


FIG. 18.—Interference Fringes on the Surface of Abraded Steel (Grade 1F emery paper): (*a*) Before and (*b*) After Electrolytic Polishing in an Industrial Cell with Aceto-perchloric Electrolyte. The dark areas on (*b*) are inclusions present in the steel. (*After Heyes*[111])

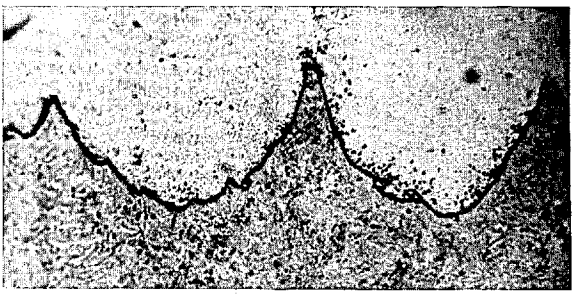
(*a*) (*b*)



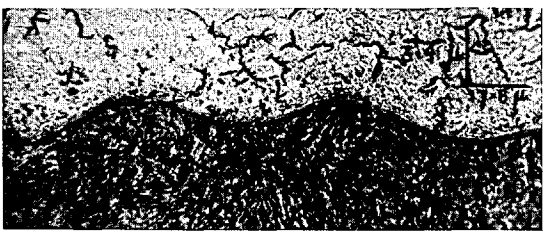
[*Courtesy "Metalloberfläche"*

FIG. 19.—Interference Fringes on Aluminium Chemically Polished by the Alupol Process. (*a*) 99·99 Al. (*b*) 99·77% Al.
(*After Lattey and Neunzig*[115])

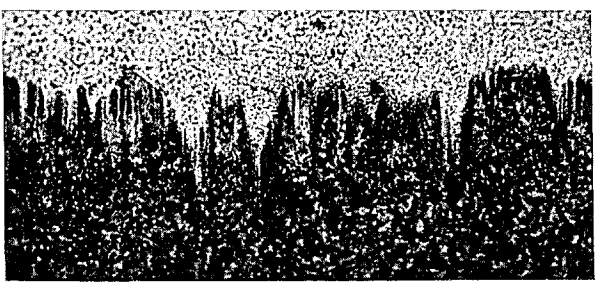
(*a*)



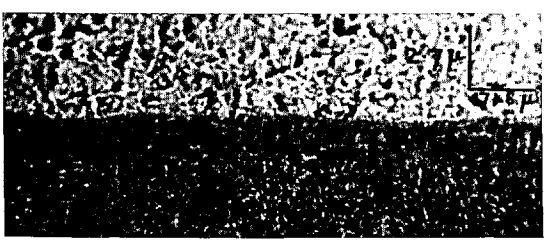
(*b*)



(*c*)



(*d*)

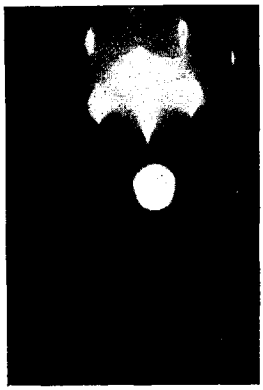


[*Courtesy "La Technique Moderne"*

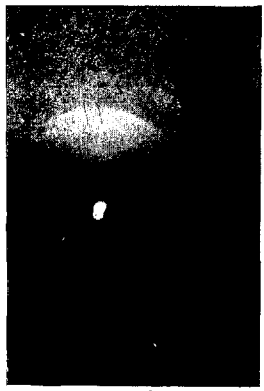
FIG. 20.—Effect of Electrolytic Polishing (by the Hispano-Suiza Superfinishing Process) on the Microgeometrical Characteristics of Cylindrical Specimens. Taper-sectioning method. Upper portion of each figure is electrolytic iron cladding. (*a*) Turned surface. Max. peak to valley = 7·5–9·5 μ. (*b*) As (*a*), but electropolished so as to reduce dia. by 50 μ. Max. peak to valley = 2·3–2·8 μ. (*c*) Ground surface. Max. peak to valley = 3·8–4·5 μ. (*d*) As (*c*), but electropolished so as to reduce dia. by 50 μ. Max. peak to valley = 0·8–1·0 μ.

Note: The surfaces (*b*) and (*d*) have the same frictional characteristics, although their microprofiles are markedly different. (*After Mondon*[196])

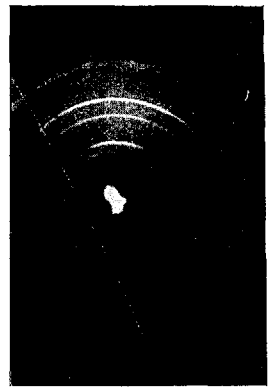
(Reduced by $\frac{1}{5}$ in reproduction)



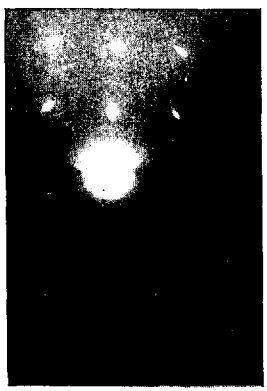
(*a*)



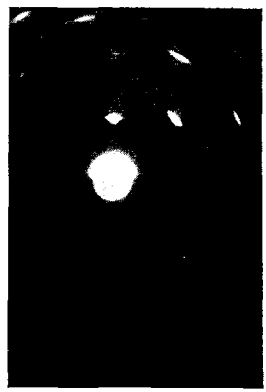
(*b*)



(*c*)



(*d*)



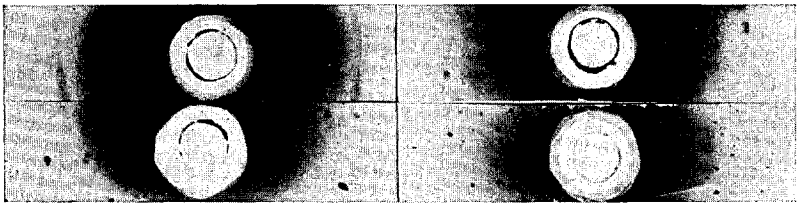
(*e*)

[*Courtesy "Annalen der Physik"*

FIG. 21.—Changes in Electron-Diffraction Patterns with Increasing Depth Below the Surface. The specimen consisted of a copper single crystal cold worked by 30 minutes' burnishing with a 0·5-cm.-radius steel ball under manual pressure of 1–2 kg.

(*a*) As electrolytically polished before burnishing. (*b*) 2000 Å. below the worked surface (crystallite dimensions about 30 Å). (*c*) 5000 Å. below the worked surface (crystallite dimensions about 50 Å). (*d*) 1–2 μ below the worked surface (fibre diagram of the crystal face). (*e*) About 10 μ below the worked surface (almost perfect diagram of a single crystal).

(*After Kranert and Raether*[148])



[*Courtesy Mme A. R. Weill and E. Mencarelli*

FIG. 22.—Back-Reflection Focused X-Ray Diagrams (Cu Radiation) Taken at Various Depths Below the Surface of Nimonic Alloy.

(*a*) Initial condition: surface abraded by a file and on emery papers as far as No. 0000. Diffuse rings show intense cold working. (*b*) After removal of 6·3 μ by electrolytic polishing. (*c*) After removal of 19 μ by electrolytic polishing. (*d*) After removal of 50 μ by electrolytic polishing.

The spots, which become increasingly clear and fine with increasing distance below the surface, correspond to grains which are progressively less disturbed.

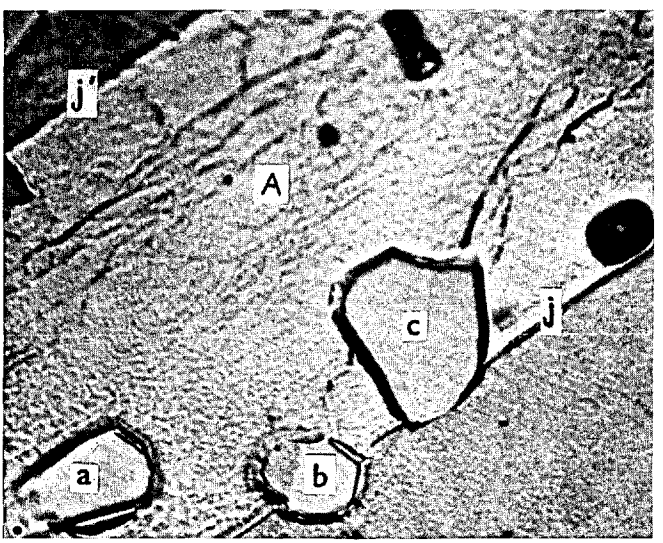
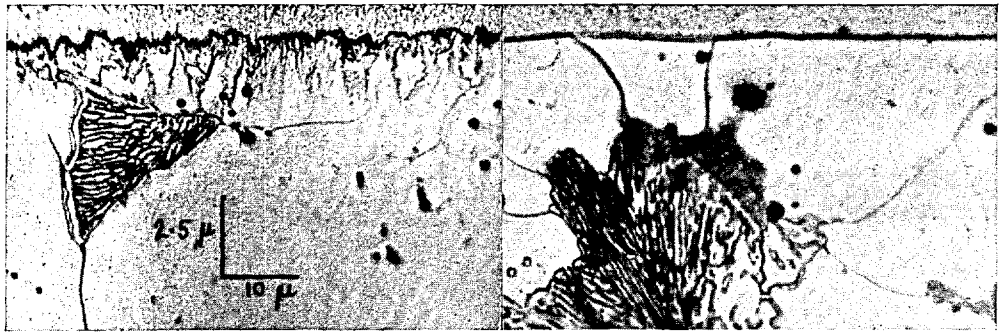


FIG. 23.—α-Brass Abraded on No. 2 Emery Paper, then Annealed for 1 hr. at 450° C. + 3 hr. at 500° C. + 1 hr. at 600° C.

Recrystallization and polygonization have occurred simultaneously to a depth of 24 μ below the surface. In spite of the high annealing temperature, the structure has not reverted to normal. (*After P. Jacquet*)

a, b, c = new crystals. jj' = boundaries of primary crystals.
A = primary crystal in which a polygonized sub-structure is formed.



[*Courtesy "Metal Finishing"*

(*a*) (*b*)

FIG. 24.—Taper Section Through the Surface of a 0·34% Carbon Steel: (*a*) abraded on No. 1 emery paper and (*b*) electrolytically polished after abrasion.

Micrograph (*a*) shows, at a depth of about 2 μ below the surface, a transgranular network in the ferrite. This is absent from (*b*) and is shown on a surface section in Fig. 25.

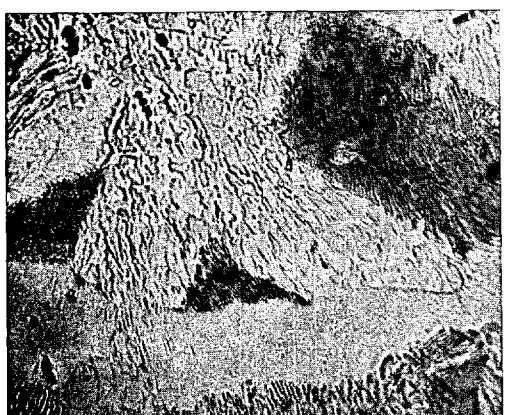


FIG. 25.—0·34% Carbon Steel. × 700. The surface was abraded on No. 2 emery paper (much coarser than No. 1) and was then polished electrolytically to dissolve about 3 μ from the surface. A sub-structural network is clearly visible within the ferrite grains. It is shown in section in Fig. 24 (*a*). (*After P. Jacquet*)

Surface

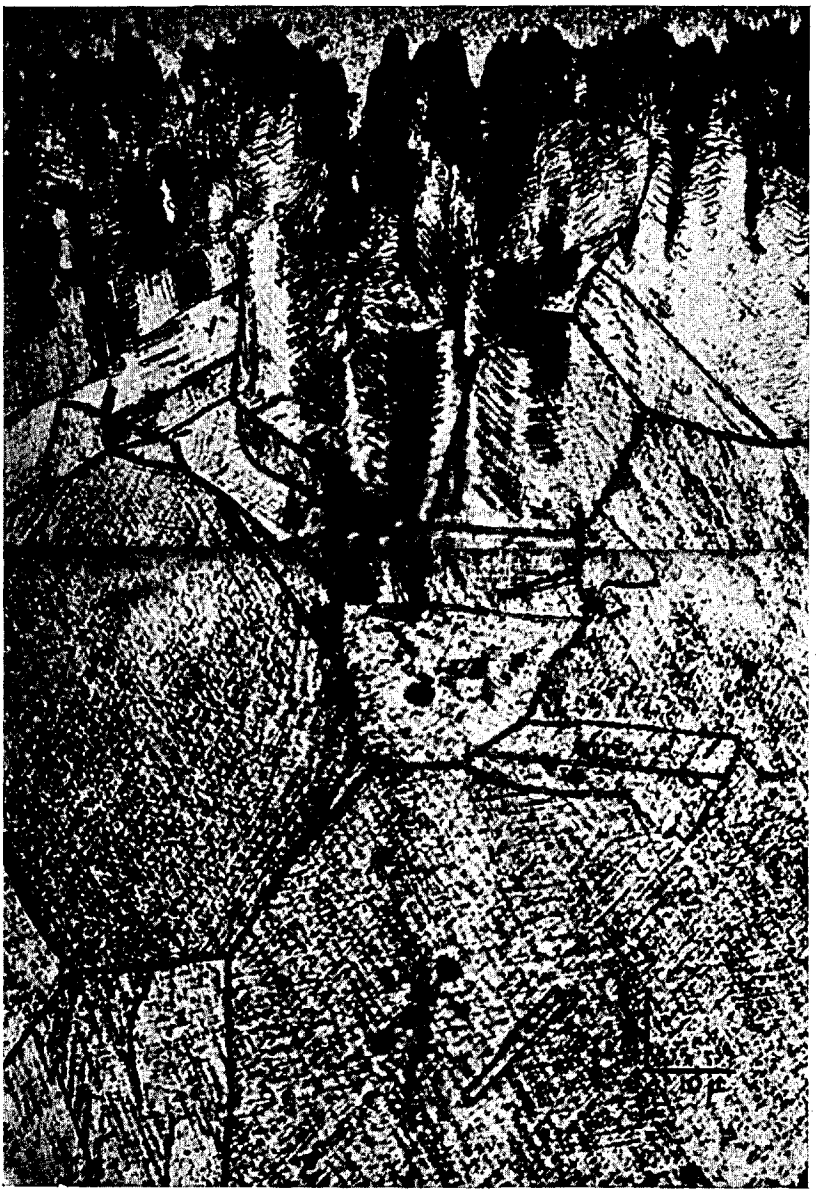
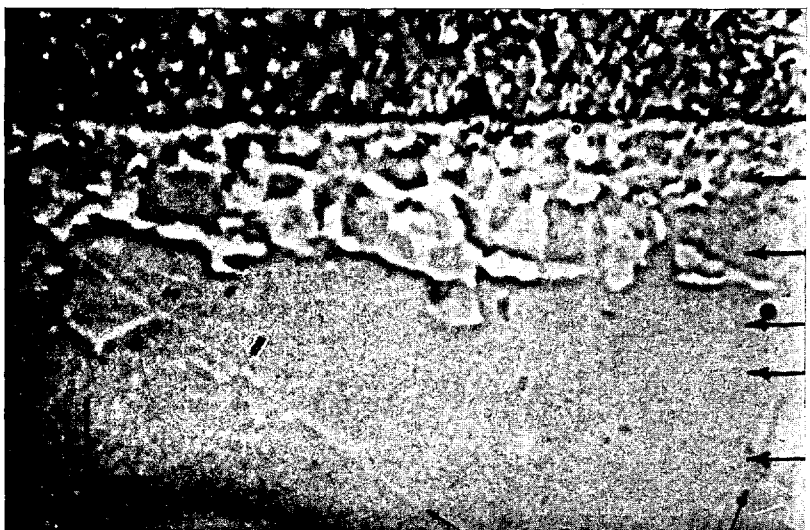


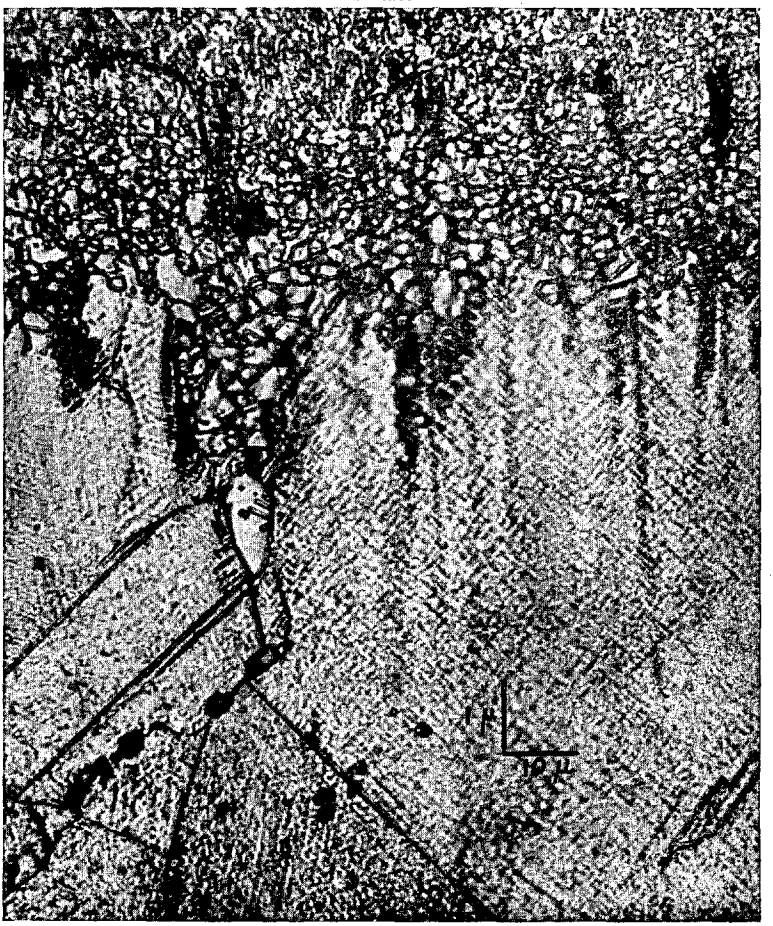
FIG. 26.—Taper Section Through the Surface of α-Brass, Abraded on No. 1 Emery Paper, and then Protected by Coating with Copper. The section was electrolytically polished for 10 hr. in order to remove any cold work due to cutting, and was then attacked anodically in a dilute solution of sodium hyposulphite. The most pronounced signs of plastic deformation correspond to the abrasion scratches and extend to a considerable depth below the surface. (*After Jacquet*)



[*Courtesy "Revue de Métallurgie"*

FIG. 27.—Taper Section Through a Surface of Pure Iron Showing Polygonization. The specimen was given a micrographic polish (emery papers as far as No. 00, then with an alumina suspension). The oblique arrows at the foot indicate two sub-boundaries of the polygonized structure. The sub-structure below the surface is of the same kind as that shown in Fig. 24(*a*) and 25. (*After P. Jacquet*[158])

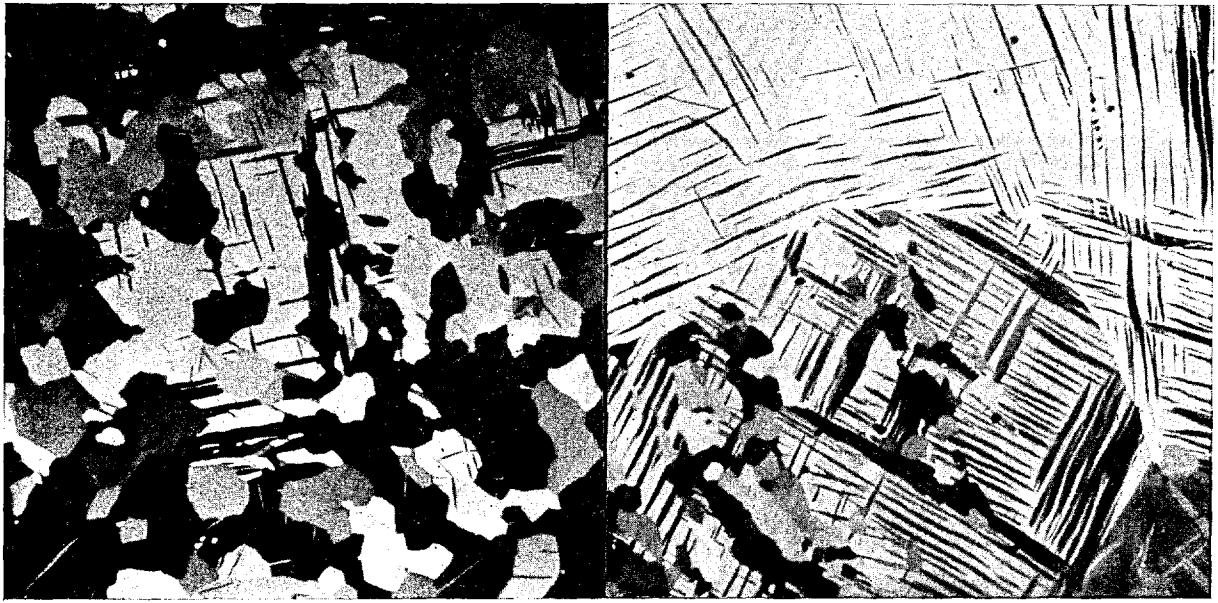
Surface



[*Courtesy "Revue de Métallurgie"*

FIG. 28.—Same Brass Specimen as Fig. 26, after Annealing for 23 hr. at 195° C. + 7 hr. at 250° C. + 1 hr. at 350° C. The superficial layer, of average thickness 4 μ, has recrystallized, but deeper regions show only slight reduction in slip lines.

(*After P. Jacquet* [156])



(*a*) (*b*) [*Courtesy "Metall"*

FIG. 29.—The Effect of Mechanical Working on the Surface of Very Pure Zinc. The surface was filed, milled, and then abraded mechanically on emery papers (No. 1 to 00000). It was then electrolytically polished in a phosphoric acid–ethyl alcohol bath and examined under polarized light at various stages.

(*a*) After removal of 40 μ. Small recrystallized grains and traces of twinning. × 160.

(*b*) After removal of 120 μ. A very few small recrystallized grains still persist. Large normal crystals are visible, heavily twinned. × 66. (*After P. Jacquet*)

FIG. 29.—(*c*) Same field as Fig. 29 (*b*) but after removal of 200 μ. Normal structure but the crystals are still distorted as is shown by the twins. × 66.

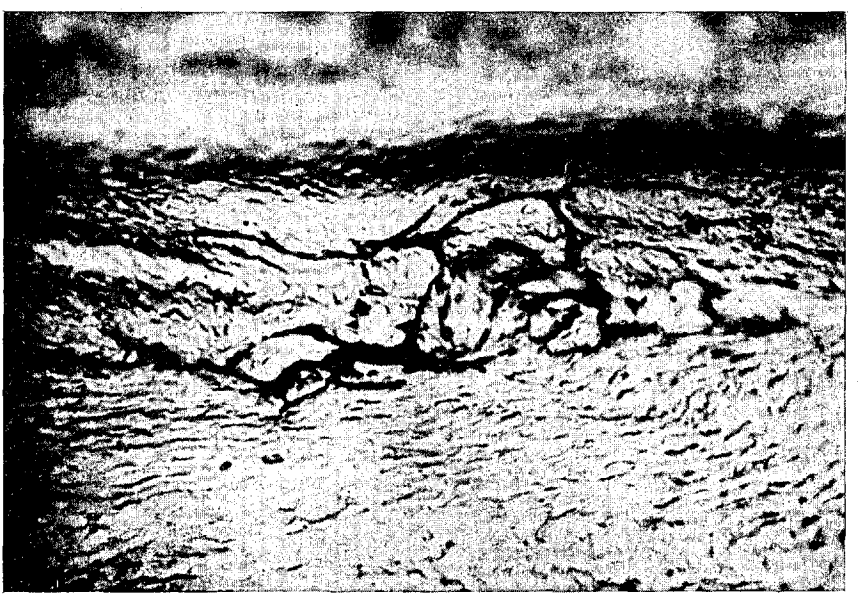


FIG. 30.—Surface of Pure Iron Abraded on No. 2 Emery Paper, and then Electrolytically Polished to Dissolve 1–1·5 μ. × 2000. Discontinuities are visible in the most heavily deformed regions. The microhardness here is of the order of 300–450 kg./mm.^{2}, as compared with about 140 kg./mm.^{2} in the regions free from cracks. (*After P. Jacquet*)

slowly into the other; the addition of anhydride to perchloric acid liberates less heat than the reverse operation, but is nevertheless not recommended because it involves the production of mixtures very rich in perchloric acid. In practice it is best to add the acid in very small amounts at a time in the anhydride, while stirring and cooling. Various pieces of apparatus have been described for making the mixture.[128]

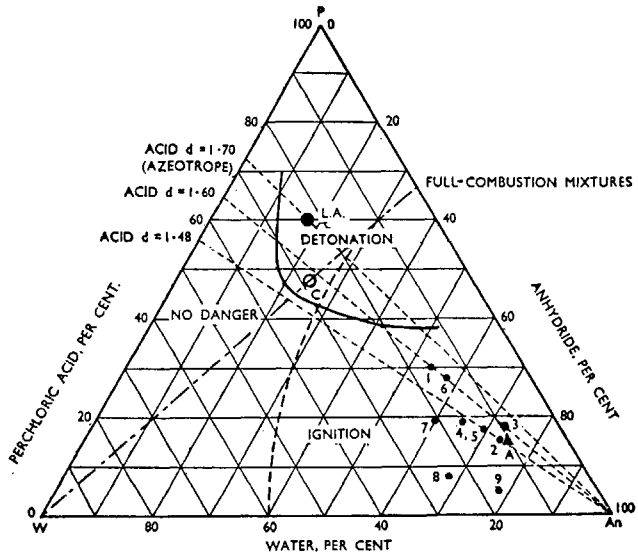


FIG. 7.—Ternary Diagram (in weight percentages) of Mixtures of Perchloric Acid (P), Acetic Anhydride (An), and Water (W).
The diagram shows:

(1) Mixture A, in which all the water contained in the perchloric acid ($d = 1{\cdot}60$) is taken up by the acetic anhydride.
(2) Mixture C—the "point of complete combustion"—which has the most pronounced explosive character.
(3) Mixture L.A. which gave rise to the explosion in the O'Connor cell at Los Angeles.
(4) Solutions numbered 1 to 9 are used for electrolytic polishing.

One proof of the absence of danger with aceto-perchloric baths is afforded by the fact that the original mixture proposed by Jacquet and Rocquet[46]—containing 185 c.c. of $HClO_4$ (60–72%), 765 c.c. acetic anhydride, and 50 c.c. water, devised for the micrographic polishing of small specimens of iron and steel—is today used on an industrial scale in Germany in forty or so plants,[129] with the authorization of the German Centre for the Prevention of Accidents.[100] Research work similar to that carried out by Médard and Sartorius has confirmed that

the mixture in question will not explode unless it is taken to a high temperature, of the order of 200° C. To make this impossible, industrial plants containing up to 1200 l. of electrolyte are fitted with a device which immediately introduces water into the bath if the temperature rises dangerously.[130]

To summarize, use in the laboratories of small quantities of electrolytes of perchloric acid and acetic anhydride leads to no special danger. The author has in fact been working for twenty years with mixtures of the kind without noticing the least tendency to fire or explosion, and so have many other investigators. Mixtures of perchloric acid and acetic acid have the advantage of being easier to prepare, with no risk of overheating.

C. COMPARISON BETWEEN CHARACTERISTICS OF SURFACES POLISHED MECHANICALLY, ELECTROLYTICALLY, AND CHEMICALLY

Electrolytic and chemical polishing give to the surface of a metal an appearance similar to that produced by traditional mechanical methods. But the fundamental differences between mechanical methods on the one hand and electrolytic and chemical methods on the other lead to the conclusion that, in spite of appearances, the characteristics of the two kinds of surface are not the same. It is even possible that electrolytic and chemical finishes may also not be identical, whilst what has been said earlier on the mechanism of these processes makes it clear that the micro- and submicro-profile, as well as the chemical properties, of the resulting surfaces depend upon the operating conditions.

Generally speaking, specimens are polished for purposes for which some or all of the surface characteristics—microgeometrical, physical, or chemical—are of great importance. It is therefore essential to know as precisely as possible what these characteristics are.

It should also be remembered that electrolytic polishing is largely responsible for recent work on the part played by surface state, since this method alone allows a study to be made of the individual effects of the factors involved.

I.—Microgeometrical Characteristics

The polished state represents, by definition, perfect smoothness on the macro-, micro-, and submicroscopic scales. Smoothness on the macro- and microscopic scales is associated with a mirror-like finish, whilst micro- and submicroscopic factors determine brilliancy.

A film of pure metal, deposited by evaporation in a vacuum on an

optically flat surface, is the best example of a mirror of high brilliance. An appearance of the same kind can be obtained by the very careful mechanical polishing, with diamond dust, of a piece of metal which is chemically and physically homogeneous. However, in this case, highly sensitive optical methods often reveal defects which are either inherent in the metal, such as inclusions and porosity, or are introduced by the polishing operation, such as scratches. A good polish can be obtained on material which is chemically heterogeneous if the phases present do not differ too greatly in hardness, and minute physical heterogeneities tend to disappear through flow of the surface layer.

An exact microgeometrical definition of a surface polished electrolytically or chemically is more difficult to formulate, because factors inherent in the material or in operating conditions preponderate. Dissolution tends to reveal, and even to exaggerate, physical defects such as porosity and cracks, and at the same time it leads to the appearance of relief effects associated with the microstructure, such as grain boundaries, inclusions, or different phases. The magnitude of these effects, and also that of a certain degree of surface waviness, depend to a great extent on the operating conditions. These general statements may be illustrated by examples quoted in the literature.

For surfaces of pure monocrystalline metals (copper and aluminium), electrolytically polished in the laboratory, electron microscopy (direct reflection at glancing incidence,[131] transmission through replicas,[131, 132]), electron diffraction,[68, 71] and adsorption isotherms[133] show that the height of the asperities and waves varies between 100 and 150 Å, though it may fall as low as a few interatomic distances, whereas a surface of aluminium, very well polished mechanically, may have asperities between 600 and 4000 Å.[131] With polycrystalline metals, very small differences in level—of the order of 20 Å.—are due to unequal rates of dissolution at different crystallographic planes; disturbances of these planes due to cold working are also apparent in the submicro-relief (see p. 181 and Fig. 13, Plate XVIII).

With pieces of steel, electrolytic polishing under industrial conditions, with an aceto-perchloric bath, has been shown markedly to improve the microprofile[134]: this is shown in Table IV and Fig. 18 (Plate XXII).

The method of taper sectioning shows in a striking manner the selectivity of electrolytic dissolution. With the Hispano-Suiza technique, the smallest asperities disappear rapidly, but, with short periods of electrolysis, a very characteristic wavy profile remains (Fig. 20, Plate XXIII).

By means of measurements and observations on the Brush Analyser, by microscopic work, and by optical-reflection methods, Faust[135] found that the grain-size of a metal has a marked influence on the improve-

TABLE IV.—*Microprofiles of Steel Components*

	Mean Microprofile, μ	
	Before Polishing	After Polishing
Finish-turned valve seats	4·0	<0·10
Finish-ground valve stems	0·35	<0·10
Crankpins	1·5	<0·08
Crankshaft	2·0	0·7

ment of the microprofile in industrial electrolytic polishing, a fine grain being more favourable than a coarse one.

The effect of composition, in the case of some steels, is shown in Table V, in which the degree of micro-relief is assessed, by the Heyes–Lueg method, by the factor K, which is the ratio between light reflected from dark-ground and clear-ground illumination.

TABLE V.—*Electrolytic Polish of Various Steels in Aceto-Perchloric Acid*[100]

Steel	$K \times 10^{-3}$	
	Before Electro-polishing	After Electro-polishing
B218 (C 0·5, Cr 1·1, V 0·17%)	119	2·93
B89 (C 0·56%)	—	3·96
CR-M (C 0·3, Cr 1·2, Ni 4·24%)	—	5·92
My (C 0·93, Mn 1·09, Cr 0·6%)	—	19·60
SS (C 1·56, Cr 3·73, V 3·24, W 15·7%)	—	1450·00

The same optical method has been used to show the effect of electro-polishing conditions. In order to obtain a given degree of improvement in the microprofile, it is necessary to reduce the thickness by 28 μ in a phosphoric–sulphuric acid bath, but by only 5 μ in one containing acetic and perchloric acids.[136]

The quality of the polish obtained on an 18:8 stainless steel containing a fine grain-boundary precipitate is extremely sensitive to polishing conditions. A mirror polish is obtained in an aceto-perchloric bath, whereas strong relief effects at the grain boundaries appear on polishing in an industrial phosphoric–sulphuric acid bath.[137] Similar effects are seen with laboratory electrolytes for polishing pure metals. The electron microscope shows that zinc is polished better in a phosphoric–ethyl alcohol bath than in 25% caustic soda solution,[138] while polishing aluminium in magnesium perchlorate–ethyl alcohol electrolyte reveals

microstructural details[139] invisible after polishing in a perchloric acid–acetic anhydride bath. It must again be emphasized that, for any bath, the conditions of electrolysis, e.g. the current density, have a marked effect on the micro-relief.[140]

Less information is available about the microgeometry of surfaces polished chemically. According to Edwards, the rate at which irregularities disappear is not very different from that in electro-polishing (Fig. 5), but published data do not present such a favourable picture (see Table VI).

TABLE VI.—*Microprofiles of Chemically Polished Materials*

Material	Ref. No.	Profilometer Measurements in micro-in. (R.M.S.)					
		Before Polishing	After Chemical Polishing for:				
			2 min.	3 min.	6 min.	50 min.	90 min.
Dull nickel plate	135	25	21	—	—	—	—
Aluminium	135	40	23	22	—	—	—
,,		80	50	50	—	—	—
70 : 30 Brass	135	30	20	24	16	—	—
,,		26	—	18	16	—	—
Mild steel	141	39	—	—	—	26	21
,,		19	—	—	—	13	12

Inclusions of other phases tend to cause pits, so that the best polish is obtained with metals of high purity (Fig. 19, Plate XXII).

Sub-microscopic chemical polishing is not as satisfactory as the polish obtained electrolytically, and the electron microscope often reveals corrosion figures.[142] More or less pronounced etching of the grains is generally visible if the bath composition has been incorrectly adjusted, for example if too much water is present.[143]

II.—PHYSICAL CHARACTERISTICS

Physical characteristics of a surface include the structure and the properties, such as hardness and residual stress, associated with it. When polishing is carried out mechanically, it generally represents the final stage in a series of operations using abrasives of increasing fineness; these disturb the structure more seriously the more severe the conditions and the lower the elastic limit of the material. Since grain boundaries are obstacles to the propagation of slip, single crystals are particularly sensitive to mechanical disturbances of the surface.

Metallographers have long known of the existence of these structural disturbances due to the mechanical preparation of their specimens, but it was not until modern methods of X-ray and electron diffraction and

optical and electron microscopy, combined with the judicious use of electro-polishing, became available, that the extent and nature of these disturbances caused in the surface layers by machining, abrasion, and polishing could be determined.

One of the early metallographers, Osmond, recognized the existence of these disturbed layers, which he designated the "cold-worked skin", and he sought to minimize their importance by the use of means such as polish-attack.[144] At the beginning of the twentieth century, Sir George Beilby started his systematic studies of the surface structure of polished materials, including metals, minerals, and glasses. By using very simple methods, he attempted to show that the final stage of polishing, which conferred on the metal its flatness and its maximum reflectivity, did not consist simply of the eradication of the last asperities, but involved also a kind of flow or viscous smearing of the superficial layers of molecules. He put forward the theory that, during friction, a very thin layer of the metal behaved as a liquid, losing its crystalline character and in fact becoming amorphous.[145] It was this surface zone that was called the "Beilby layer".

The first electron-diffraction experiments gave rise to lively controversy. The two diffuse diffraction rings generally seen in the patterns from polished metals were believed by some investigators to afford proof of the amorphous nature of the surface, whereas others regarded them as being due to a superficial oxide film.

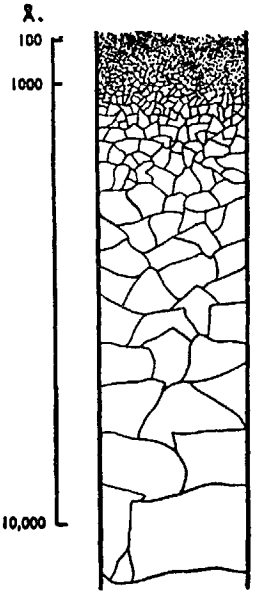
Finch and his co-workers believed that they had formal proof of the amorphous nature of the Beilby layer,[146] but it appears that no-one has ever been able to reproduce their results.[131]

Although it was not concerned with a metal, an important fact reported by Kranert and Raether on selenium[147] merits consideration. This element gives rise to two different diffraction patterns, one corresponding to the crystalline and the other to the amorphous state. After mechanical polishing, crystalline selenium retains this pattern, the only difference being that the size of the crystals is greatly reduced.

The same authors[148] have studied the changes which appear in a series of electron-diffraction diagrams taken at increasing depths below the surface—the (100) plane—of a single crystal of copper, initially polished mechanically by 30 minutes' burnishing with a steel ball under alcohol. Before taking each diagram, the surface was exposed by chemical or electrolytic solution in phosphoric acid.

The results (Fig. 21, Plate XXIV) show that the size of the crystals decreases continuously as the zone examined approaches the surface. The extreme surface zone, 50 Å. thick, consists of fragments of about 5 Å. dia., but it is impossible to say whether they are elementary crystallites or amorphous or vitrified particles. In any case, on this

scale, distinction between these different states becomes meaningless. The important point is that beneath this thin skin the single crystal is subdivided into crystallites increasing in size until ultimately they merge into the undisturbed lattice. Fig. 8 gives a schematic view of the



[*Courtesy "Annalen der Physik"*

Fig. 8.—Diagrammatic Representation of the Surface Layers as Deduced from the Electron-Diffraction Patterns of Fig. 21 (Plate XXIV). (*After Kranert and Raether*[148].)

structure which Kranert and Raether deduced from their diagrams (Fig. 21, Plate XXIV).

X-ray diffraction diagrams give similar results, but as X-rays are considerably more penetrating than electrons, the diagrams cannot give such a detailed picture of the structure. They are most suitable in cases of severe cold work caused by abrasion or by the use of tools. With abraded single crystals of aluminium, copper, and iron, the Laue spots are replaced by Debye–Scherrer rings, and do not reappear until a considerable depth of metal has been dissolved away,[149] and the same applies to polycrystalline specimens.[150, 158] For example, Fig. 22 (Plate XXV) shows a series of X-ray diagrams taken during the anodic polishing of a specimen of Nimonic alloy, which was first abraded with a fine file and afterwards with emery papers of increasing fineness.

By micrographic techniques of great sensitivity, applied either to the surfaces themselves or to taper sections, it is possible to reveal the structural disturbances caused by abrasion and polishing. α-brass (Fig. 26, Plate XXVII) and pure iron and ferrite in carbon steel (Figs. 24, 25, Plate XXVI, Fig. 27, Plate XXVIII) lend themselves particularly well to this type of experiment.[151] With brass, after abrasion, the top layer, 1–2 μ thick, has a confused microstructure which cannot be resolved. Below this appear slip bands typical of plastic deformation, which extend to a greater depth the more severe the abrasion. After use of a No. 1 emery paper, they may reach 40 μ in depth. With pure iron and ferrite in carbon steel, after a micrographic polish, the disturbances do not take the form of slip bands, but result in a cellular network resembling polygonization.

Since the disturbed layers are due to plastic deformation of the crystals, they should be harder than the bulk of the material and should recrystallize on annealing. Surface hardening is well known to those studying microhardness;[152] it is clearly revealed on a taper section (Fig. 27, Plate XXVIII) or on the surface itself after a series of electrolytic polishing operations. This method is extremely sensitive for determining the exact thickness of the cold-worked layers (Table VII).

TABLE VII.—*Determination of Thickness of Cold-Worked Layer on Various Materials*

Metal	Polishing Conditions	Thickness of metal (μ) which has to be removed before the normal microhardness is restored.
Copper single crystal[153]	Burnishing with agate ball for :	
	5 min.	4
	15 ,,	10
	30 ,,	80
Aluminium single crystal[154]	Micrographic	100
Polycrystals[152] :		
Quenched hard steel	Micrographic	2– 5
Very mild steel	,,	15– 20
Copper and silver	,,	30– 80
Aluminium	,,	50–150

The recrystallization of the surface layers on annealing has long been known in the case of abraded α-brass,[155] but recent improvements in micrographic technique have led to a more thorough investigation.[156] The kinetics of recrystallization are not the same at different depths below the surface, since the degree of cold work decreases with depth.

At first only the top layer (1–2 μ thick) recrystallizes (Fig. 28, Plate XXIX), followed later by a part of the next lower zone. Below that the deformation is not sufficiently severe to permit nuclei of new grains to appear, even at a high temperature, and the dislocations form polygonization boundaries. In intermediate zones, recrystallization and polygonization can exist simultaneously (Fig. 23, Plate XXV).

It is possible for recrystallization to occur during mechanical polishing and abrasion, owing to the heat developed by friction.[157] This is particularly so in the case of metals whose recrystallization temperature is near to room temperature. For instance, micrographs of the surface of a coarse-grained specimen of very pure zinc (Fig. 29 (*a*), (*b*), Plate XXX, and Fig. 29 (*c*), Plate XXXI) show deformation marks (twins) and also small crystals.

Certain observations have led to the suspicion that the mechanical properties decrease in the superficial layers cold worked by abrasion or by tools.[135] Micrographs of iron and carbon steels indeed show signs of discontinuities quite clearly, in the form of very fine cracks up to 1–2 μ below the surface (Fig. 30, Plate XXXI). These discontinuities occur in the regions where the microhardness reaches a maximum, and they certainly tend to show that the ultimate tensile stress of the material has been exceeded during the mechanical working.[158]

Finally, it must be mentioned that abrasion and mechanical polishing are capable of producing phase transformations. For instance, in 18:8 stainless steel, 90% of the austenite in a layer $2{\cdot}5 \times 10^{-5}$ cm. thick is transformed into ferrite, and the unaltered austenite is found only below 4×10^{-5} cm.[159] Again, abrasion of a single crystal of pure iron on a 0000 emery paper causes the appearance of the γ phase on the surface, indicating the attainment of a temperature in excess of 900° C., followed by an almost instantaneous quench.[160]

To summarize: from the moment when the surface of a metal is subjected to the mechanical operations of abrasion, working by tools, or polishing, for the purpose of improving its microprofile, it acquires a new structure which changes with increasing depth below the surface and eventually merges into the normal structure. The degree of structural disturbance, and the thickness of the zones affected, depend on the nature of the metal, on its metallurgical state, and on the conditions under which it was worked.

Since the properties of the metal are modified in the surface zones, these zones should be removed in all investigations in which the state of the surface is of primary importance, and electrolytic polishing has proved to be the best method of achieving this object. Before its discovery, either chemical dissolution or high-temperature annealing had to be used. The first of these methods was certainly efficacious, but it

caused a considerable deterioration in the quality of the surface, quite incompatible with a polished finish. The second method eliminated the cold-worked structure, but did not necessarily bring about a return to the normal structure, as has been seen in the case of α-brass (Fig. 28, Plate XXIX, Fig. 23, Plate XXV). Moreover, such annealing must be carried out in a vacuum or in a neutral atmosphere in order to avoid chemical contamination.

The unique advantage of electrolytic polishing lies in its ability to dissolve the disturbed layers completely, whatever their thickness, whilst maintaining or even improving the microgeometrical features of the surface. Chemical polishing has the same effect, but it cannot be recommended in the case of thick layers.

The absence of structural disturbances on the surface of metals polished electrolytically was first shown, indirectly, by simple means such as the crystal continuity between a cathodic deposit and its support.[155, 161] It has been confirmed by X-ray and electron diffraction,[149, 162] whilst the perfection of the lattice of an electrolytically polished single crystal has been clearly demonstrated by the sharpness of the Kikuchi lines.[160, 163]

In all investigations in which it is essential that the specimen shall be freed from even the least trace of distortion, the duration of electrolytic polish must be sufficient to remove the entire thickness of the layers affected by the previous mechanical operations, and in fact every endeavour should be made to avoid such operations. For instance, test-pieces should be electro-machined,[105] and annealed specimens should be electro-polished directly; such precautions are particularly important in the case of single crystals.[164]

Plastic deformation of a metal sets up internal strains,[165] the distribution of which can be determined by progressively dissolving away the surface layers by anodic polishing.[166] It is well known that such strains invariably result from mechanical working of the surface, as for instance in machining, flattening, abrasion, or polishing, &c.[167] The fact that they can be removed by electrolytic polishing accounts for the effect, mentioned previously, of this method of finishing on the fatigue properties of the material.[168]

III.—Chemical Characteristics

The contamination of metallic surfaces exposed to the atmosphere is a common phenomenon leading to the formation of solid films of oxides or sometimes sulphides. Under the usual conditions of abrasion and mechanical polishing, oxidation cannot be avoided, as is shown by electron diffraction.[169] With iron and steel, superficial formation of

nitrides has even been detected.[170] Such contamination can be minimized by excluding air during the mechanical operations, for instance, by working under benzene.

The passivity of some metals which are not noble (e.g. chromium and stainless steel) is no doubt due to the presence of a very thin film of oxide or of adsorbed oxygen, though its mechanism is still debated, in spite of the considerable number of investigations that have been carried out. Hatwell[171] has shown that after abrasion in the absence of air (in an argon atmosphere) alloys of iron containing 3–25% chromium have a constant solution potential, measured again in the absence of air. After exposure to air, alloys containing at least 12% chromium show an ennoblement of the surface, with a potential characteristic of the passive state. In this case, therefore, passivation is not an intrinsic property of alloys rich in chromium, but results from oxidation, which begins only at a certain chromium content.

1. *Electrolytic Polishing*

It is difficult to define precisely the chemical nature of a metal polished electrolytically, because examination, whether by electron diffraction, solution potential, electrolytic reduction, or micro-analysis, must be done after the specimen has been removed from the polishing bath, washed with liquids such as water, alcohol, acetone, &c., and exposed to the atmosphere. It has also been shown that the operating conditions, such as composition of the electrolyte, current density, and applied voltage, are capable of affecting the chemical state of the surface during polishing. These two groups of factors, which may be termed external and internal, may explain the contradictory results reported by various investigators.

The first experiments were made on the assumption that all metals polished electrolytically were covered with a film of oxide.[172] Careful investigation has shown, however, that this does not hold in all cases, and that chemical compounds, other than oxides, may cause contamination.

(*a*) *Aluminium*

Lacombe and his collaborators[173] have established the relationship between the solution potential of metal polished in the Jacquet bath and the presence of an oxide film which forms in contact with air. In every case, even if this contact is reduced to a minimum, the potential is −1·20 V., which still differs considerably from the theoretical value. If atmospheric action is suppressed completely, both during and after polishing, the value reaches the theoretical (about −1·60 V.).

According to Raether, electron diffraction is less sensitive than solution potential for detecting thin oxide films, but more sensitive for thick ones.[174] In fact, a surface which has a solution potential of —1·20 V. gives the diffraction pattern of pure aluminium, free from oxide; at least 40–50 Å. thickness of alumina must be present before its characteristic pattern appears. This is the case if the metal is exposed to air. If aluminium is polished in other electrolytes, such as phosphoric acid–chromic acid or perchloric acid–methyl alcohol, the alumina pattern is observed, and the solution potential falls to —0·76 V. which is identical with that for aluminium mechanically polished.[68] It is therefore possible to say that, subject to certain conditions respecting the age of the bath, and the temperature, polishing in the Jacquet bath gives an aluminium surface completely free from oxide, but extremely susceptible to oxidation on exposure to air or to the liquids used for washing. On the other hand, with other electrolytes, the metal is already covered with oxide during polishing.[68, 69, 70, 73]

With certain aluminium alloys, another kind of surface contamination is possible. For instance, with aluminium–copper alloys,[175] a thin film of copper may be deposited, formed by chemical replacement in the viscous anolyte layer.

(*b*) *Copper*

Halfawy has specified the conditions required in order to obtain the diffraction pattern of the unoxidized metal.[176] This, however, does not exclude the possible presence of a film of cuprous oxide, a few atoms thick.

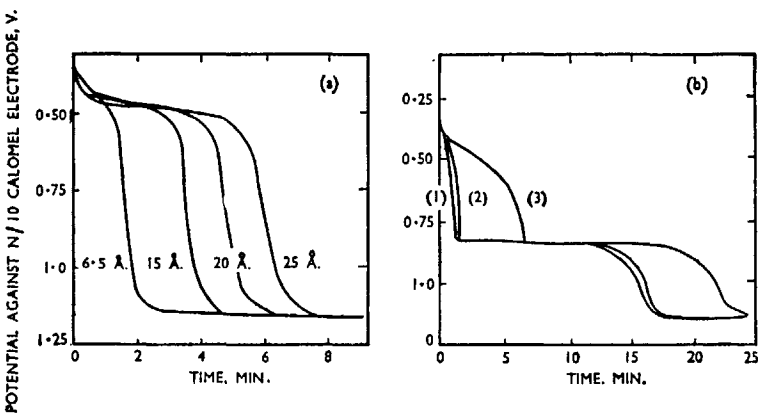
Quantitative micro-analysis of a large number of specimens polished in orthophosphoric acid solution (1000 g./l.) has shown that in 60% of them there is a film of phosphorus-bearing compounds, of the order of 0·25–0·5 γ P_2O_5/cm.^{2} Conditions under which the sample is washed, on leaving the electrolyte, are important factors bearing on this type of contamination,[177] as electrochemical-reduction potential measurements show[178] (Fig. 9).

With copper alloys rich in zinc, electron-diffraction diagrams indicate surface dezincification,[179] the cause of which is not known.

(*c*) *Zinc*

As in the case of aluminium, the nature of the electrolyte is of great importance. The Jacquet solution (phosphoric acid–ethyl alcohol) is the only one giving metal with a solution potential approaching the equilibrium value.[180] Raether states that the electron-diffraction pattern corresponds neither to zinc nor to the oxide, and he postulates the presence of a passivating film, 40 Å. thick, containing both oxide

and solution products.[181] Micro-analysis confirms that 81% of these specimens are covered with a film containing compounds of phosphorus (0·1–0·5 γ P_2O_5/cm.^{2}).[177]



[*Courtesy Faraday Society*

FIG. 9.—Application of the Campbell and Thomas Electrolytic Reduction Method to a Determination of the Thickness of the Cu_2O Film produced on Copper when Electrolytically Polished in H_3PO_4 (d = 1·34 approx.).

(*a*) The specimen was washed in distilled water and rinsed in a solution of 10% phosphoric acid, then in alcohol.

The film of thickness 6·5 Å. was obtained with a surface washed in liquids free from oxygen and transferred to the apparatus while still moist with alcohol. That having a film 15 Å. in thickness was produced by drying with filter paper and exposing to the air for 30 min. The two thicker films—20 and 25 Å.—correspond to longer times of exposure to air.

(*b*) The specimen was washed as for (*a*) but the 10% phosphoric acid rinse was omitted. The potential plateau at —0·83 V. is possibly due to a film of basic phosphate of copper (cf. ref. 177).

(*After Allen*[178].)

(*d*) *Other Metals*

Some information is available on the chemical nature of the surface of iron, 18:8 stainless steel, magnesium, nickel, titanium, uranium, and cadmium, electrolytically polished in various solutions.

Finch and his colleagues[160, 163] have published some very beautiful diagrams of single crystals of iron polished in the Jacquet–Rocquet aceto-perchloric bath, indicating that the surface is pure. However, Cohen,[182] working with polycrystalline iron, obtained evidence of traces of γ-Fe_2O_3, and the electron microscope appeared to confirm the presence of an oxide film.[183] The solution potential corresponded to the passive state, but for some unknown reason some of the specimens

were active.[180] From Tolley's experiments,[173] it seems probable that, like aluminium, iron acquires an oxide film after polishing. Armco iron, polished in an industrial phosphoric acid–chromic acid bath, is definitely passive, the film containing neither chromium nor phosphorus.[177]

Stainless steel (18:8) is passivated in industrial phosphoric–chromic and phosphoric–sulphuric baths.[184(a)] The passivating film produced in the Jacquet aceto-perchloric bath, if it exists at all, is extremely thin, but it increases in thickness very rapidly in contact with air, as is shown by its behaviour towards certain reagents.[137]

The remarkable degree of passivation shown by iron–chromium alloys polished electrolytically has found application in the manufacture of some kinds of Geiger–Müller counters with improved characteristics.[184(b)]

Magnesium, polished in the phosphoric acid–alcohol bath, is invariably rendered passive by a solid film which probably contains oxide, hydroxide,[185] and anodic products rich in phosphorus.[177]

Nickel is rendered passive in electrolytic polishing baths, particularly with certain compositions.[186]

The very high reactivity of titanium towards oxygen leads to the supposition that passivation should be easy. A surface freshly polished in an aceto-perchloric bath gives a correct micrographic etch in boiling dilute sulphuric acid, but if the specimen is exposed to the air for several hours, the etching is not satisfactory.[187] This behaviour is very similar to that of 18:8 stainless steel.

The electron-diffraction pattern of uranium polished in a phosphoric acid–sulphuric acid bath shows evidence of an oxide.[188] With monocrystalline cadmium, polished in a perchloric acid–alcohol bath, the pattern is that of the pure metal.[189]

2. *Chemical Polishing*

Little has been published on the purity of chemically polished surfaces. The Miley–Evans method, involving the measurement of potential during cathodic reduction, indicates the presence of a film of oxide on the surface of iron containing 0·1% carbon, chemically polished in the oxalic acid–hydrogen peroxide bath developed by Marshall.[72] Although the experiment was made with the minimum exposure to the atmosphere, oxidation subsequent to polishing cannot be ruled out. The film has, however, an appreciable thickness (45 Å., calculated as Fe_2O_3) and other facts support the view that the mechanism of polishing may well involve the formation of an oxide film.

Bolognesi,[190] by comparing aluminium polished electrolytically in the Jacquet bath and chemically in a mixture of acids, found that in *N*-HCl, in the presence of mercury, the electrolytic surface was attacked more rapidly than the chemical.

3. *Cleaning Treatments after Polishing*

Films of chemical compounds, such as oxides or salts, are obviously harmful in investigating surface phenomena such as oxidation, corrosion, and catalysis. When their presence on electrolytically or chemically polished specimens is suspected, many methods are available for removing them.

(*a*) *Dissolution*

The reagent should dissolve the film rapidly without appreciable attack on the metal. A phosphoric acid–chromic acid solution is used to remove oxide from aluminium[191]; orthophosphoric acid is similarly used for copper,[192] and various reagents are known for use with other metals.[193]

(*b*) *Thermal Treatment*

This is carried out in a vacuum or in hydrogen, and can only be used if structural changes do not occur, or if such changes are unimportant for the work envisaged. Instances are investigations on single crystals, and oxidation at high temperatures,[194] respectively.

(*c*) *Cathodic Evaporation in Hydrogen*

This method[195] could be more widely used, for it has pronounced advantages, such as great efficiency, the avoidance of serious heating, and the complete preservation of the polished surface.

4. *Conclusions*

Improvement, by purely mechanical means, of the microgeometry of the surface, with its ultimate aim of producing a perfect mirror finish, is incompatible with the retention of the normal structure of the surface layers, and with the chemical cleanliness of the surface. By replacing the mechanical process by one involving dissolution, the electrolytic and chemical processes preserve the crystal lattice of the surface unaltered, whilst conferring smoothness and remarkable brilliancy.

Provided that the composition of the bath and the operating conditions are correctly chosen, and that certain precautions are taken in manipulating the specimens, electrolytic polishing generally assures chemical cleanliness sufficient for a very large number of applications. When the absence of all traces of impurity is an absolute necessity, methods of treatment, after polishing, are now available.

General Conclusions

As might have been expected from the original experiments made some twenty years ago, electrolytic polishing has proved to be a method

which is almost indispensable for work on a range of problems concerning either directly or indirectly, the surface of a metal. The rational use of this method, and of the chemical method to which it led, has gone considerably beyond the initial, largely empirical stage. In fact, a critical study of the very numerous publications shows the existence of very varied trends, reflecting, no doubt, the predominant interests of the authors.

The present author has attempted to classify the results obtained—some of which are still debatable—from the point of view of a metallographer rather than that of an electrochemist. But these two standpoints, chemical and metallurgical, cannot be entirely separated. The possibility of scientific uses of surfaces polished by the new techniques depends to a great extent on the characteristics of these surfaces, and these characteristics themselves depend on the operating conditions adopted. There is a certain tendency to regard electrolytic and chemical polishing merely as simple tools, comparable with those of the mechanic or the wheel of the polisher. It is hoped that the present account has succeeded in showing that the complexity of the phenomena which accompany and follow the production of a polished surface does not justify such a view.

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APPENDIX I

Table of Electrolytic Polishing Conditions
Most Frequently Used for Small Specimens

(1) All references to acetic acid imply the undiluted glacial acid.
(2) The abbreviations used are as follows: d = density; t = temperature (°C.); V = voltage at the terminals of the cell; C.D. = density of anodic current (amp./cm.²); A=amp. I = current in ampères (in the case of the Disa-Electropol apparatus, where the anodic surface area is in general 0·4 cm.²); T = duration of electrolysis.
(3) The references are given at the end of the table.

Electrolyte Composition	Conditions	Remarks	References
	I.—*Aluminium and its Alloys*		
200 c.c. perchloric acid (d = 1·60) 700 c.c. acetic anhydride	C.D. = 0·2–0·4 (according to the composition of the alloy)	Preliminary enrichment of the electrolyte with Al^{+++} (5g./l.)	99
345 c.c. perchloric acid (d = 1·55–1·60) 655 c.c. acetic anhydride	t < 25° V = 15–30 C.D. = 0·04	—	1, 103
125 c.c. perchloric acid (d = 1·60) 875 c.c. acetic anhydride	t = 20–25° V = 15–25 (for specimen 2 cm.²) T = several min.	Stainless-steel cell (18:8) serving as cathode	104
230 c.c. perchloric acid (d = 1·54) 770 c.c. acetic acid	t = 5° V = 15–32 (according to the composition of the alloy) T = 5 min.	—	127
100 c.c. perchloric acid 400–500 c.c. ethyl alcohol (or methyl alcohol)	t < 30° V = 10–15 C.D. = 0·15–0·20	—	2, 122

200 c.c. perchloric acid ($d = 1{\cdot}20$) 700 c.c. ethyl alcohol 100 c.c. butylcellosolve	V = 40–50 T = 15–30 sec.	Disa-Electropol	4
400 c.c. orthophosphoric acid ($d = 1{\cdot}78$) 380 c.c. ethyl alcohol 200 c.c. water	t = 30–40° V = 27–30 C.D. = 0·15–0·35	Conditions rather critical, varying with the age of the bath. Applicable to Al–Ag alloys. Possible formation of a film of alumina	101
By vol. 53% orthophosphoric acid ($d = 1{\cdot}69$) 26% water 20% carbitol 1% hydrofluoric acid (48%)	V = 80 initially, then 40 when C.D. reaches 0·6. If C.D. is too low, a thick film of alumina forms T = 2–3 min.	Large volume of bath and stirring required	111
By vol. 40% orthophosphoric acid 50% ethyl alcohol 10% glycerol	—	Simultaneous polishing and anodic oxidation	3
By vol. 60% orthophosphoric acid ($d = 1{\cdot}69$) 40% sulphuric acid ($d = 1{\cdot}84$)	t >70° C.D. = 0·7	—	6
817 c.c. orthophosphoric acid ($d = 1{\cdot}57$) 134 c.c. sulphuric acid ($d = 1{\cdot}84$) 156 g. chromic acid 40 c.c. water	t = 70° V = 14 (before immersion of specimen)	For Al–Cu alloys. Formation of an alumina film removed in cold phospho-chromic solution	100
100 c.c. nitric acid (68–70%) 200 c.c. methyl alcohol	V = 4–7 C.D. = 0·1–1 T = 10 sec.–2 min.	Buehler apparatus or cell. Danger of explosion (?)	5, 114
100 c.c. conc. nitric acid 100 c.c. methyl alcohol 4 c.c. conc. hydrochloric acid	V = 5; Al cathode	For electrolytic thinning, the HCl diminishes the tendency to oxidation	110

Electrolyte Composition	Conditions	Remarks	References
	II.—*Beryllium*		
28 c.c. perchloric acid ($d = 1{\cdot}60$) 200 c.c. acetic anhydride	t = <28° C.D. = 0·1	Slow stirring of the bath	11
200 c.c. perchloric acid ($d = 1{\cdot}20$) 700 c.c. ethyl alcohol 100 c.c. butylcellosolve	V = 40–50 T = 20 sec. V = 50 C.D. = 0·75–0·90 T = 30–45 sec.	Disa-Electropol Cell has a horizontal anode; rapid stirring is necessary	65
3 parts conc. orthophosphoric acid 1 part chromic acid	V = 50 C.D. = 2·5	Pb or graphite cathode. Poisonous fumes	9
100 c.c. conc. orthophosphoric acid 30 c.c. sulphuric acid 30 c.c. glycerol 30 c.c. ethyl alcohol (99°)	C.D. = 2–4	—	10
	III.—*Bismuth*		
100 c.c. orthophosphoric acid 200 c.c. sulphuric acid 200 c.c. water	C.D. = 1	—	10
100 c.c. acetic acid 100 c.c. nitric acid 400 c.c. glycerol	t = 24° V = 12 T = 1–5 min.	—	9
Saturated solution of KI to which has been added 20 c.c./l. HCl	V = 7 C.D. = 0·2	Solid film which disappears some seconds after the current has been cut off	12
Ammonium thiocyanate (60%)	C.D. = 0·5		13

IV.—*Cadmium and its Alloys*			
200 c.c. perchloric acid ($d = 1{\cdot}60$) 800 c.c. acetic anhydride	t = 35–55° V = 25–35 C.D. = 0·6–1	Cd cathode. Conditions depend upon the age of the bath	107
200 c.c. perchloric acid ($d = 1{\cdot}20$) 700 c.c. ethyl alcohol 100 c.c. butylcellosolve	V = 70–80 T = 12–15 sec.	Disa-Electropol. Suitable for alloys containing Ni, Ag, or Cu	11
450 c.c. orthophosphoric acid 550 c.c. water	V = 2 C.D. = 0·05–1·5	Agitation of specimen recommended	14
Per litre: 120 g. potassium cyanide 20 g. cadmium hydroxide	V = 2·8 C.D. = 0·12–0·25 T = 15 min.	Separation of the electrodes 20–30 mm. Vigorous gas evolution	15
V.—*Chromium*			
50 c.c. perchloric acid ($d = 1{\cdot}60$) 1000 c.c. acetic acid	V = 35–45 C.D. = 0·15	—	9, 16
200–300 c.c. perchloric acid ($d = 1{\cdot}60$) 800–700 c.c. acetic acid	V = 10–12 C.D. = 0·2–0·4	For solid solutions of Fe and Cr at any Cr concentration	113
By vol. 64% orthophosphoric acid 15% sulphuric acid 21% water	t = 22–120° V = 18 C.D. = 1·5	Stirring of the bath or agitation of the specimen	17
Aqueous solution containing 95% orthophosphoric acid	—	—	17

Electrolyte Composition	Conditions	Remarks	References
	VI.—*Cobalt and its Alloys*		
304 c.c. perchloric acid ($d = 1{\cdot}60$) 696 c.c. acetic anhydride	—	For Co–Ni alloys, reduce the concentration of perchloric acid	18
240 c.c. perchloric acid 750 c.c. acetic acid 20–30 c.c. water	$V = 30$	For the alloy Alnico	19
Solution of orthophosphoric acid ($d = 1{\cdot}35$)	$V = 1{\cdot}2$	Black solid film. Pitting possible	10, 20
	VII.—*Copper and its Alloys*		
Solution of orthophosphoric acid ($d = 1{\cdot}30$–$1{\cdot}44$)	$V = 1{\cdot}6$–$1{\cdot}8$ C.D. $= 0{\cdot}7$–1	Horizontal anode Vertical anode Can be used for electro-machining under special conditions	21 129
Solution of orthophosphoric acid ($d = 1{\cdot}70$)	$V = 1{\cdot}75$–$1{\cdot}80$ C.D. $= 0{\cdot}015$	For brasses containing Pb	11
Solution of orthophosphoric acid ($d = 1{\cdot}61$)	$V = 4{\cdot}3$ C.D. $= 0{\cdot}08$ $V = 2$–$2{\cdot}2$	For Al bronzes For nickel silver	22 117
260 c.c. orthophosphoric acid 740 c.c. glycerol	$t = 40$–$50°$ $V = 45$–60 C.D. $= 0{\cdot}04$ $T = 14$–20 min.	For polishing Cu_2O	26
370 c.c. orthophosphoric acid 560 c.c. glycerol 70 c.c. water	$t = 50$–$70°$ C.D. $= 0{\cdot}15$	For nickel silver	116

470–670 c.c. orthophosphoric acid 20– 10 c.c. sulphuric acid 33– 23 c.c. water	V = 1·8–2·2 C.D. = 0·1	For Sn bronzes	25
100 c.c. conc. nitric acid 200 c.c. methyl alcohol	C.D. = 0·7	The Buehler–Waisman apparatus could possibly be used	9, 23, 108
Solution of chromic acid (200 g./l.)	C.D. = 1–2·5	—	24

VIII.—*Germanium*

500 c.c. glycerol 50 c.c. ethyl alcohol (95°) 50 c.c. water Add acid potassium fluoride to form saturated solution	t = 20° C.D. = 0·01 T = 30 min. t = 80° C.D. = 0·1	—	34
Solution of 0·1 N-indium sulphate or chloride (pH = 1·2–3·5)	C.D. = 3	Can be used only for very small specimens (reduction in thickness of transistors)	35
Fused mixture of sodium chloride–potassium chloride (48 mol.-%)	t = ⩾660° V = 2	Large Pt cathode; etching of crystals	34, 124

IX.—*Gold and its Alloys*

Per litre: 67·5 g. potassium cyanide 15 g. Rochelle salt 18·5 c.c. orthophosphoric acid (d = 1·69) 2·5 c.c. ammonia (d = 0·9)	t > 60° V = 5–10 C.D. = 1–1·5	Violent agitation. Cu cathode. Very slow speed of solution	51
0·5% gold chloride (or hydrochloric acid) 10% potassium cyanide	V = 1·5 C.D. = 0·15–0·20	Pure graphite cathode. Specimen agitated. Vapours poisonous when HCl is used	52
25 g. thiourea 3 c.c. sulphuric acid (d = 1·84) 10 g. acetic acid	t = 20–45° C.D. = 0·015–0·035	—	53

Electrolyte Composition	Conditions	Remarks	References
	X.—*Hafnium*		
100 c.c. acetic acid 5 c.c. perchloric acid	V = 18 I = 0·4 (for very small specimens)	Repeated electrolysis of short duration	36
	XI.—*Indium*		
100 c.c. conc. nitric acid 200 c.c. methyl alcohol	C.D. = 0·3	—	37
50 c.c. conc. nitric acid 20 c.c. conc. hydrochloric acid 750 c.c. carbitol	V = 40–60 C.D. = 0·3—0·6	Al cathode. Applicable to alloys containing Tl. The solid film should be removed by 10% hydrofluoric acid. The bath can be used for polishing at 100° the In–Tl phase stable at high temp. Cathode of 18:8 stainless steel	38, 130
	XII.—*Iron and Steel*		
185 c.c. perchloric acid (d = 1·60) 765 c.c. acetic anhydride 50 c.c. water	t = <30° C.D. = 0·04–0·06 T = 3–5 min.	The solution should preferably contain a small amount of Fe or Al. Of all the baths, this one has the max. throwing power	9, 29, 33, 109
480 c.c. perchloric acid (d = 1·60) 520 c.c. acetic anhydride	t = 5° V = 25 C.D. = 0·5 T = 2–4 min.	For polishing FeO	26
1000 c.c. acetic acid 50 c.c. perchloric acid (d = 1·60)	t < 25° V = 25–45 C.D. = 0·1–0·2	Slight agitation. Conditions depend on the age of the bath	16

1000 c.c. acetic anhydride 140 c.c. perchloric acid ($d = 1{\cdot}60$)	V = 20–40	Slight agitation. Microstructure lightly revealed	11
100 c.c. perchloric acid 400 c.c. methyl alcohol	—	Cooling and agitation	31
200 c.c. perchloric acid 700 c.c. ethyl alcohol 100 c.c. butylcellosolve (or glycerol)	V = 40–47 A = 1 T = 10–20 sec.	Disa-Electropol. Can be used for ferro-Si with high Si content	4
36 c.c. perchloric acid ($d = 1{\cdot}67$) 97 c.c. water 500 c.c. methylated spirit	C.D. = 0·3–1	Specimen horizontal above the cathode	32, 33
By weight: 80% acetic acid 20% chromic acid	C.D. = 0·5–2	—	33
133 c.c. acetic acid 25 g. chromic acid 7 c.c. water	C.D. = 0·09–0·22 T = 6 min.	For ferro-Si	92, 94
900 g. orthophosphoric acid ($d = 1{\cdot}69$) 100 g. chromic acid	t = 90° C.D. = 1·55	Cu cathode. For 4% ferro-Si	30, 93
420 c.c. orthophosphoric acid ($d = 1{\cdot}69$) 340 c.c. sulphuric acid ($d = 1{\cdot}84$) 240 c.c. water	Source 6 V. The metal container acts as a cathode. 0·03 amp. per needle. Alternating immersion and withdrawal of 15–20 mm.	For making very fine needles in stainless steel. Cleaning in 10% hydrochloric acid	112
500 c.c. conc. nitric acid 500 c.c. acetic acid	C.D. = 1·5–3 T = 10–20 sec.	—	33
100 c.c. orthophosphoric acid (maximum concentration) 100–150 g. ammonium sulphate	t = 200–350° V = 20 C.D. $\geqslant$ 0·6 T = 10 sec.–3 min.	Polishing at high temp. for austenitic structures, isothermally heated	118
100 c.c. aqueous solution of 10% ammoniacal copper chloride 300 c.c. conc. hydrochloric acid	V = 70 C.D. = 200 A = 1·4	For the electro-machining of test-pieces with a jet of electrolyte	129

Electrolyte Composition	Conditions	Remarks	References
	XIII.—*Lead and its Alloys*		
350 c.c. perchloric acid ($d = 1{\cdot}60$) 325 c.c. acetic anhydride 25 c.c. water	V = 5–8 C.D. = 0·09–0·14	Precautions in washing and drying the specimen	9, 55
700 c.c. acetic acid 300 c.c. perchloric acid ($d = 1{\cdot}67$)	V = 10 C.D. = 0·4–0·6 T = 2–5 min.	Applicable to alloys of low Ag content	42, 58
100 c.c. perchloric acid ($d = 1{\cdot}12$) 400 c.c. ethyl alcohol (96°)	t < 38° C.D. = 2–3	Variable conditions depending on composition of specimen	9, 56
315 c.c. acetic acid 60 g. anhydrous sodium acetate 80 c.c. water	C.D. = 0·05–0·10 $T \geqslant 4$ min.	Graphite or Pt cathode	57
Aqueous solution of 40% fluoboric acid	t = 20–40° V = 16–21 C.D. = 3·7–7 T = 3–5 sec.	Variable conditions depending on composition of specimen	91
Aqueous solution of 70–80% ammonium acetate	C.D. = 0·5–0·1	—	13
	XIV.—*Magnesium*		
375 c.c. orthophosphoric acid ($d = 1{\cdot}71$) 625 c.c. ethyl alcohol (95°)	V = 1·5 C.D. = 0·005	Adhesion of gas bubbles must be avoided	9, 39, 95, 96
400 c.c. orthophosphoric acid ($d = 1{\cdot}75$) 380 c.c. ethyl alcohol (absolute) 200 c.c. water	V = 10 C.D. = 0·2 T = 2 min.	Mg cathode. Specimen withdrawn whilst the current is on	102

10% hydrochloric acid in solution of butylcellosolve	$t \leqslant 10°$ $V = 10$–15 C.D. $= 0{\cdot}015$	Initial increase of voltage	40
10 c.c. conc. hydrochloric acid 135 c.c. carbitol	C.D. $= 0{\cdot}10$–$0{\cdot}15$	After a preliminary electrolysis, dissolve the passivating film in KOH	10
XV.—*Manganese (Alloys)*			
100 c.c. orthophosphoric acid ($d = 1{\cdot}69$) 100 c.c. glycerol 200 c.c. ethyl alcohol	C.D. $= 0{\cdot}3$–$0{\cdot}5$ $T = 15$ min.	For Cu alloys. Specimen withdrawn very quickly and washed in alcohol	41
100 c.c. orthophosphoric acid 200 c.c. sulphuric acid 200 c.c. water		For alloys with 2·5. at-% U	10
XVI.—*Molybdenum*			
870 c.c. sulphuric acid ($d = 1{\cdot}84$) 30 c.c. water	C.D. $= 0{\cdot}5$	Oxide film removed by 3% CrO_3 solution	42
35 c.c. sulphuric acid ($d = 1{\cdot}84$) 140 c.c. water	$t = 50°$ $V = 12$	For sintered Mo without C. Oxide film removed with ammonia	43
25 c.c. sulphuric acid ($d = 1{\cdot}84$) 175 c.c. methyl alcohol	$t < 25°$ C.D. $= 0{\cdot}8$–$1{\cdot}2$	Precautions are necessary in preparing the solution	44
50–60 c.c. conc. hydrochloric acid 20–30 c.c. sulphuric acid ($d = 1{\cdot}84$) 150 c.c. methyl alcohol	$t = 50°$ $V = 12$	For cast Mo without C.	43, 120
Aqueous solution of 70% potassium thiocyanate	C.D. $= 0{\cdot}15$		13

Electrolyte Composition	Conditions	Remarks	References
	XVII.—*Nickel and its Alloys*		
210 c.c. perchloric acid ($d = 1{\cdot}60$) 790 c.c. acetic acid or anhydride	With acid bath C.D. = 0·5–0·8 With anhydride bath t < 35° C.D. = 0·18	—	42, 45
40 c.c. perchloric acid ($d = 1{\cdot}60$) 450 c.c. acetic acid 15 c.c. water	t < 25° V = 15 C.D. = 0·10	For Nimonic alloys	47
200 c.c. perchloric acid ($d = 1{\cdot}20$) 700 c.c. ethyl alcohol 100 c.c. glycerol (or butylcellosolve)	V = 40 A = 1	Disa-Electropol	4
70 wt.-% sulphuric acid	V = 10–25 C.D. = 0·28–1	Stirring of bath	46, 106
390 c.c. sulphuric acid ($d = 1{\cdot}84$) 290 c.c. water	t < 35° C.D. = 0·39 T = 4–6 min.	Gives better results than the preceding bath	115
390 c.c. sulphuric acid ($d = 1{\cdot}84$) 70 c.c. ethyl alcohol	C.D. = 0·4	Precautions are necessary in preparing the solution	9
By weight: 15% sulphuric acid ($d = 1{\cdot}84$) 64% orthophosphoric acid 21% water	t = 70° V = 2·5–2·8	For Nimonic alloys	48
10 c.c. conc. nitric acid 20 c.c. methyl alcohol	C.D. = 0·75–1·5 T = several sec.	Disa-Electropol or a small cell. Can be used for Inconel, Monel, and Ni–Cr alloys	23
133 c.c. acetic acid 25 g. chromic acid 7 c.c. water	C.D. = 0·23–0·29	For alloys with a high Fe content	125

XVIII.—*Niobium*			
175 c.c. hydrofluoric acid (40%) 175 c.c. nitric acid (d = 1·384) 650 c.c. water	V = 12–30 C.D. = 0·2–0·5	Cell is a Pt crucible serving as a cathode	49
150 c.c. hydrofluoric acid (48%) 850 c.c. sulphuric acid (d = 1·84)	t = 25–60° C.D. = 0·04	Pt cathode	50
XIX.—*Palladium*			
Sodium chloride or potassium chloride	t = 950° V = 3 C.D. = 1	Closed cell, working in a current of H	54
Sodium chloride + 48 at.-% potassium chloride	t = 700° V = 2	Polishing of large areas possible	34
XX.—*Platinum*			
Sodium chloride or potassium chloride	t = 1020° V = 1·5 C.D. = 0·15	Cell is a Ni crucible serving as a cathode	54
Sodium chloride + 48 at.-% potassium chloride	t = 700° V = 2	Pt cathode	34
Aqueous solution of calcium chloride (120 parts by weight) + 1 part hydrochloric acid	A.C. (50 c./s.) V = 3	For small specimens	34

Electrolyte Composition	Conditions	Remarks	References
	XXI.—*Silver*		
Solution of 9% potassium cyanide	C.D. = 2	Strong agitation of the specimen. Wash 5 min. in cold water	121
60 g. potassium ferrocyanide 60 g. sodium cyanide 1 l. water	V = 6 C.D. = 0·15–0·25	—	7
Per litre: 35 g. silver cyanide 37–70 g. potassium cyanide 38–40 g. potassium carbonate	V = 2·5–3·5 C.D. = 0·02 T = 10 min.	Close control of C.D. and of stirring. Ag cathode. Applicable to alloys containing Sn	8, 105
200 c.c. perchloric acid (d = 1·20) 700 c.c. ethyl alcohol 100 c.c. glycerol	A = 1·5 T = 20 sec.	Disa-Electropol. Max. speed of stirring	4
	XXII.—*Tantalum*		
90 c.c. sulphuric acid (d = 1·84) 10 c.c. hydrofluoric acid (48%)	t = 35–45° C.D. = 0·1	Graphite or Pt cathode	59
100 c.c. hydrofluoric acid (48%) 100 c.c. nitric acid (d = 1·42) 350 c.c. water	t = 35–50° C.D. = 0·02–0·15	Periodic oscillations of the current due to a solid film	60

XXIII.—*Thorium*

70 c.c. acetic acid 20 c.c. perchloric acid ($d = 1{\cdot}64$) 5 c.c. water	t = 10° C.D. = 0·6 T = 7–12 sec.	—	63
20 c.c. perchloric acid ($d = 1{\cdot}54$) 90 c.c. ethyl alcohol 90 c.c. butylcellosolve	Variable conditions	Polishing and reduction of wire diameter	62
500 c.c. orthophosphoric acid 500 c.c. acetic acid	C.D. > 0·16	—	10, 61

XXIV.—*Tin and its Alloys*

Aqueous solution of perchloric acid (60%) ($d = 1{\cdot}54$)	C.D. = 0·4 T = 10–15 sec.	Cooled Al cathode. Specimen to be rotated	28
194 c.c. perchloric acid ($d = 1{\cdot}60$) 806 c.c. acetic acid	C.D. = 0·09–0·15	Moderate stirring. Specimen to be withdrawn while current is still on	9, 27
200 c.c. perchloric acid ($d = 1{\cdot}20$) 700 c.c. ethyl alcohol 100 c.c. butylcellosolve	A = 1·5 T = 20 sec.	Disa-Electropol	4
Fluoboric acid solution (40%)	V = 15–17 C.D. = 4·2–5·6 T = 3–5 sec.	Applicable to alloys containing Pb	91
Aqueous solution of sulphuric acid (35 wt.-%)	V = 30 C.D. = 0·13	Al cathode. Stirring. Specimen withdrawn while the current is still on, washed in running water and wiped	106

Electrolyte Composition	Conditions	Remarks	References
	XXV.—*Titanium and its Alloys*		
795 c.c. acetic anhydride 185 c.c. perchloric acid ($d = 1{\cdot}60$) 48 c.c. water	V = 40–60 C.D. = 0·2–0·3	Specimen lightly agitated. Face to be polished placed horizontally, beside or above the cathode	64
200 c.c. acetic anhydride 10 c.c. perchloric acid	$t \leqslant 40°$ C.D. = 1 T = 4 min.	The polished surface becomes rapidly passive in air	119
1000 c.c. acetic acid 60 c.c. perchloric acid ($d = 1{\cdot}60$)	C.D. = 0·3 T = 3 min.	Large-area Ti cathode. Excellent electric contact with the specimen is essential	126
200 c.c. perchloric acid ($d = 1{\cdot}20$) 350 c.c. ethyl alcohol 100 c.c. butylcellosolve	V = 30 C.D. = 0·018–0·035 T = 20 sec.	Disa-Electropol or cell	65, 66
36 c.c. perchloric acid ($d = 1{\cdot}67$) 390 c.c. methyl alcohol 350 c.c. ethylene glycol 24 c.c. water	t = 5–10° V = 30–50 T = 10–40 sec.	Disa-Electropol	68
90 c.c. ethyl alcohol 10 c.c. *M*-butyl alcohol 6 g. aluminium chloride (anhydrous) 28 g. zinc chloride (anhydrous)	t = 25–30° V = 30–60 C.D. = 0·16–0·8	Very corrosive solution (not to be employed in commercial apparatus). Stirring required	67
By weight 6% hydrofluoric acid 88% ethylene glycol 6% water	t = 25–40° C.D. = 0·08–0·1	Applicable to alloys containing Mn and Al	69
160 c.c./l. hydrofluoric acid (50%) 500 g./l. chromic acid	$t \leqslant 15–20°$ V = 3–7 C.D. = 0·2–0·5	Possible to use on commercial scale	70
80 c.c. glycerol 5 g. barium fluoride 5 c.c. sulphuric acid ($d = 1{\cdot}84$)	V = 90 C.D. = 0·4	—	9

XXVI.—*Tungsten*

Aqueous solution of caustic soda 10–120 g./l.	*V* and C.D. are variable, depending upon the concentration of the bath and the apparatus	Cathode = 18:8 stainless steel or Pt. Applicable to the production of fine points and the reduction of wire diameter	72, 73
Sodium orthophosphate 160 g./l.	$t = 43 \pm 3°$ C.D. = 0·39	For reduction of wire diameter	123

XXVII.—*Uranium and its Alloys*

200 c.c. perchloric acid ($d = 1·20$) 700 c.c. ethyl alcohol 100 c.c. butylcellosolve	$V = 40$ $I = 0·50$ $T = 20$ sec.	Disa-Electropol	128
20 c.c. perchloric acid ($d = 1·54$) 90 c.c. ethyl alcohol 90 c.c. butylcellosolve	Variable conditions	For reduction of wire diameter	62
50 c.c. orthophosphoric acid 100 c.c. sulphuric acid ($d = 1·84$) 100 c.c. water	$t = 15°$ C.D. = 0·1–0·75	Agitation or wiping of the surface necessary. Can be used with Disa-Electropol	75, 76
100 c.c. orthophosphoric acid 100 c.c. ethyl alcohol (absolute) 100 c.c. glycerol	C.D. = 0·1–0·2	—	75
50 c.c. orthophosphoric acid 80 c.c. ethyl alcohol 50 c.c. ethylene glycol	$t = 21°$ $V = 18–20$ C.D. = 0·01 $T = 5–15$ min.	—	9, 96
20 c.c. sulphuric acid ($d = 1·84$) 80 c.c. methyl alcohol A few drops of water	$V = 10–20$ $T =$ a few sec.	For alloys containing >30% V	78
100 c.c. chromic acid solution (84 g./100 c.c. water) 300 c.c. acetic acid	$V = 50$ C.D. = 3·20 $T = 30–60$ sec.	Suitable for alloys containing <30% Ti and V	9, 97

Electrolyte Composition	Conditions	Remarks	References
	XXVII.—*Uranium and its Alloys—contd.*		
10 g. pyrophosphoric acid 10 g. chromic acid 40 c.c. orthophosphoric acid ($d = 1{\cdot}71$) 100 c.c. sulphuric acid ($d = 1{\cdot}84$) 200 c.c. water	C.D. = 0·50 T = 5 min.	Inclusions of oxide relatively unattacked	77
	XXVIII.—*Vanadium*		
5–10% solution of perchloric acid in acetic acid	C.D. = 0·15–0·23 T = 1–2 min.	Possibility of pitting	79
10 c.c. perchloric acid ($d = 1{\cdot}60$) 100 c.c. methyl alcohol 60 c.c. butylcellosolve	V = 30 T = 7 periods of 3 sec. repeated without withdrawing the specimen	Disa-Electropol. Max. speed of stirring	80
20 c.c. sulphuric acid ($d = 1{\cdot}84$) 80 c.c. methyl alcohol A few drops of water	V = 10–20 T = a few sec.	—	78
	XXIX.—*Zinc and its Alloys*		
100 c.c. perchloric acid ($d = 1{\cdot}48$) 900 c.c. acetic acid	C.D. = 0·15–0·20	C.D. relatively critical, but has to be determined	81
100 c.c. perchloric acid ($d = 1{\cdot}12$) 400 c.c. ethyl alcohol (96°)	t < 38° C.D. = 0·8 for pure Zn; variable for the alloys	Applicable to alloys containing Al, Cu, Pb	9, 56
Aqueous solution of orthophosphoric acid ($d = 1{\cdot}375$)	V = 2·5 T = 5 min.	Shows the presence of traces of Pb in Zn	98
375 c.c. orthophosphoric acid ($d = 1{\cdot}71$) 625 c.c. ethyl alcohol	V = 2–3·5 C.D. = 0·015–0·020 V = 6 C.D. = 0·05	Very slow rate of solution	9, 39, 82, 83
Aqueous solution of chromic acid at 200 g./l.	C.D. = 2·6	—	24

200 g./l. chromic acid 15 g./l. sodium sulphate	C.D. = 2·6–7	Cooled solution. Electrodes spaced at 12–25 mm.	84
Aqueous solution of caustic potash (25%)	t = 24–30° V = 2·5–6 C.D. = 0·15–0·5 T = 5 min.	Agitation by air or N. Conditions extremely critical	9, 85
XXX.—*Zirconium and its Alloys*			
100 c.c. acetic acid 50 c.c. perchloric acid (d = 1·60)	V = 60 C.D. = 0·6–0·8	Vigorous agitation of the specimen	86, 87
175 c.c. acetic acid 50 c.c. perchloric acid (d = 1·60) 100 c.c. ethylene glycol	C.D. > 1	—	10
10 c.c. perchloric acid (d = 1·60) 100 c.c. methyl alcohol 60 c.c. butylcellosolve	V = 30 A = 1 T = 3–15 sec.	Disa-Electropol. Max. speed of stirring	80
20 c.c. perchloric acid (d = 1·54) 90 c.c. ethyl alcohol (absolute) 90 c.c. butylcellosolve	Variable conditions	For reduction of wire diameter	62
20% solution of hydrofluoric acid in ethyl alcohol	—	For alloys containing U	88
20 c.c. hydrofluoric acid 10 c.c. nitric acid 200 c.c. glycerol	t = 24° V = 9–12	—	9
100 c.c. hydrochloric acid 300 c.c. ethyl alcohol	C.D. = 1 T = 10–20 sec.	—	89
XXXI.—*Graphite*			
Acid potassium fluoride	t = fusion of the bath V = 130 C.D. = 0·1–1 T = 1 min.–1 hr.	—	90

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APPENDIX II

Principal Methods of Chemical Polishing

Bath Composition	Operating Conditions	References
	I.—*Aluminium*	
By vol. 70% orthophosphoric acid ($d = 1{\cdot}5$) 12% acetic acid 15% water	t = 100–120° T = 2–6 min.	W. R. Meyer and S. H. Brown, *Proc. Amer. Electroplaters' Soc.*, 1949, **36**, 163
By vol. 30–60% orthophosphoric acid ($d = 1{\cdot}71$) 60–30% sulphuric acid ($d = 1{\cdot}84$) 5–10% nitric acid ($d = 1{\cdot}50$) 70–90% orthophosphoric acid ($d = 1{\cdot}71$) 25–5% sulphuric acid ($d = 1{\cdot}84$) 3–8 % nitric acid ($d = 1{\cdot}50$)	t = 95–120° (according to the composition). Gas copious Suitable for preliminary polishing t = 85–110° (according to the composition). Formation of a viscous layer Suitable for final polishing	J. Hérenguel and R. Segond, *Rev Mét.*, 1951, **48**, 262 J. Hérenguel, *Metal Treatment*, 1951, **18**, 539; *Rev. Aluminium*, 1953, (**201**), 261
3 parts orthophosphoric acid ($d = 1{\cdot}59$) 1 part sulphuric acid ($d = 1{\cdot}84$)	t = 100–120° T = 2 min. After rinsing Al_2O_3 is dissolved in H_2SO_4 3% (by vol.) + CrO_3 112 g./l. t = 60–80°	C. E. Naylor, *Plating Notes*, 1951, **3**, 59
By vol. 80% orthophosphoric acid ($d = 1{\cdot}70$) 15% acetic acid ($d = 1{\cdot}05$) 5% nitric acid ($d = 1{\cdot}42$) 0·2 g./l. cetylpyridine bromide	t = 80–90° T = 2–5 min. tank: 18:8 stainless steel	B. E. Bunce, *Metal Finishing*, 1954, **52**, (1), 70
1000 c.c. orthophosphoric acid ($d = 1{\cdot}60$) 100 c.c. hydrogen peroxide (30%)	t = 90–100° T = 2–3 min.	P. H. Margulies, *Iron Age*, 1955, **175**, (4), 71
	II.—*Beryllium*	
By weight 75% orthophosphoric acid 5% sulphuric acid 7% chromic acid remainder—water	t =49°. Rate of solution 1·5 μ/min. The passivating film is removed in 10% sulphuric acid, at 25°C.	J. G. Beach and C. L. Faust, *J. Electrochem. Soc.*, 1953, **100**, 276

Bath Composition	Operating Conditions	References
III.—*Cadmium*		
Per litre of water: 45 g. hydrogen peroxide (30%) 7·5 g. sulphuric acid ($d = 1·84$)	—	P. H. Margulies, *Iron Age*, 1955, **175**, (4), 71
IV.—*Copper*		
By vol. 55% orthophosphoric acid ($d = 1·75$) 25% acetic acid 20% nitric acid ($d = 1·40$)	$55° < t < 80°$	Battelle Development Corp. (H. A. H. Pray, I. Igelsrud, and G. L. Simard) U.S. Patent No. **2,446,060**, 1948
By vol. 55% acetic acid 15% orthophosphoric acid ($d = 1·71$) 30% nitric acid ($d = 1·40$) By vol. 66% acetic acid 17% orthophosphoric acid ($d = 1·71$) 17% nitric acid ($d = 1·40$)	$t = 85°$ For copper. Rate of solution = 0·07–0·1 mm./min. $t = 50°$ For brasses with 58–90% copper and 1% tin. Rate of solution = 0·003–0·005 mm./min.	A. Varsavsky, L. A. Boschi, and J. A. Sabato, *Cuivre, Laitons, Alliages*, 1955, (**23**), 45
V.—*Germanium*		
5 parts conc. nitric acid 3 parts hydrofluoric acid (48%) 3 parts acetic acid 0·1 parts bromine (Reagent C.P–4)	t = ordinary T = 1–2 min.	J. R. Haynes and W. Shockley, *Phys. Rev.*, 1951, [ii], **81**, 835; F. L. Vogel, *Acta Met.*, 1955, **3**, 245
VI.—*Hafnium*		
45 c.c. conc. nitric acid 8–10 c.c. hydrofluoric acid (48%) 45 c.c. water		F. M. Cain, *Zirconium and Zirconium Alloys (Amer. Soc. Metals)*, **1953**, 176
VII.—*Iron and Steel*		
Per litre: 500 g. chromic acid 150 c.c. sulphuric acid	t = ordinary temp. or slightly above. Slight agitation. Rate of solution = 0·03 mm./hr. Applicable up to 0·5% carbon	G. E. Gardam, "Protection and Electrodeposition of Metals" (Selected Government Research Rep., Vol. 3), p. 133. **1951**: London (H.M. Stationery Office)

Bath Composition	Operating Conditions	References
	VII.—*Iron and Steel—contd.*	
By vol. 30 parts nitric acid (d = 1·33) 70 parts hydrofluoric acid (d = 1·12) 300 parts water	t = 60°	L. Beaujard, *Compt. rend.*, 1952, **234**, 440
2·5 g. oxalic acid 1·3 g. hydrogen peroxide 0·01 g. sulphuric acid Make up with water to 100 c.c.	t = ordinary temp. T = 1 hr. Rate of solution = 0·01 mm./hr. Applicable up to 0·4% carbon	W. A. Marshall, *J. Electrodepositors Tech. Soc.*, 1952, **28**, 27; *Research*, 1954, **7**, 89 A. Hickling and A. J. Rostron, *Inst. Metal Finishing, Preprint No.* **7**, 1955
By weight: 30% hydrochloric acid 40% sulphuric acid 5·5% titanium tetrachloride 24·5% water	For stainless steels. t = 70–80° $TiCl_4$ acting as depolarizer against H. Surfaces obtained not passive	H. H. Uhlig, U.S. Patent No. **2,172,421** 1941
	VIII.—*Lead*	
70 parts acetic acid 30 parts hydrogen peroxide	—	R. C. Gifkins, *J. Inst. Metals*, 1952–53, **81**, 417; 1953–54, **82**, 39
	IX.—*Magnesium*	
10% nitric acid in methyl alcohol — nitric acid or conc. hydrochloric acid	—	R. Grall, *Rev. Mét.*, 1955, **52**, 603 H. B. Pulsifer, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, **1928**, 461
	X.—*Nickel*	
By vol. 100 parts: { 42·5% orthophosphoric acid (d = 1·71) 42·5% acetic acid 15% nitric acid (d = 1·42) 3 parts sulphuric acid (d = 1·84) 15 parts water	t = 80–10°	Battelle Development Corp. (H. A. H. Pray, I. Igelsrud and G. Simard), U.S. Patent No. **2,446,060**, 1948

Bath Composition	Operating Conditions	References
	X.—*Nickel—contd.*	
By vol. 60–70% acetic acid 40–30% conc. nitric acid 0·5% conc. hydrochloric acid	t = ordinary T = 15–30 sec.	L. P. Fox, U.S. Patent No. **2,680,678**, 1954
20 c.c. acetic acid 10 c.c. nitric acid 4 c.c. hydrochloric acid	For alloy: 77% Ni–14% Fe–5% Cu–4% Mo	R. E. S. Walters, *Acta Met.*, 1954, **2**, 890
	XI.—*Silver*	
Aqueous solution of sodium cyanide + hydrogen peroxide (to be prepared immediately before use)	$t < 32°$ Alternating immersion in the bath and in sodium cyanide solution at 37·5 g./l.	Quoted by R. Pinner, *Electroplating*, 1953, **6**, 407
	XII.—*Tantalum*	
2 parts acetic acid 5 parts sulphuric acid 1 part hydrofluoric acid	—	D. A. Vermilyea, *Acta Met.*, 1954, **2**, 476
	XIII.—*Titanium*	
8–10 c.c. hydrofluoric acid (48%) 60 c.c. hydrogen peroxide (30%) 30 c.c. water	T = 30–60 sec.	F. M. Cain, *Metal Progress*, 1953, **63**, (5), 174
Pyrophosphoric acid	$t = 270 \pm 10°$ At the end of the bath immerse in orthophosphoric acid (d = 1·74) cold, then in cold water	H. W. Worner, *Bull. Inst. Metals*, 1954, **2**, 131
	XIV.—*Zinc*	
By weight 22% chromic acid 2·5% sulphuric acid 1·5% acetic acid 74% water	After 2 min. in the solution, immerse for 10 sec. in 10% potassium hydroxide	J. J. Gilman, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 1217
160 g. chromic acid 20 g. sodium sulphate (crystals) 500 c.c. water	t = ordinary temp. T = 10 sec. Slight agitation of the specimen	J. J. Gilman, *Acta Met.*, 1955, **3**, 277

Bath Composition	Operating Conditions	References
	XIV.—*Zinc—contd.*	
Per litre : 200 g. chromic acid 15–30 g. sodium sulphate 50–85 c.c. nitric acid	$t = 20°$ $T = 3$ min. Rate of solution = 0·4 mm./hr. The solution must be frequently replaced	W. Vinaver and P. Dreulle, *Rev. Mét.*, 1955, **52**, 612 L. Boschi, H. Destaillats, J. Sabato, J. Walls, and A. Varsavski, *Métaux Corrosion-Ind.*, 1955, **30**, 108
By weight : 2–5% hydrogen peroxide 2–5% sulphuric acid	$T = 30$ sec.	P. H. Margulies, *Iron Age*, 1955, **175**, (4), 71
	XV.—*Zirconium*	
45 c.c. conc. nitric acid 8–10 c.c. hydrofluoric acid (48%) 45 c.c. glycerol	$T = 5$–10 sec. after the appearance of fumes. For Zr and alloys of low content	F. M. Cain, *Zirconium and Zirconium Alloys* (*Amer. Soc. Metals*), **1953**, 176
45 c.c. hydrogen peroxide 45 c.c. conc. nitric acid 8–10 c.c. hydrofluoric acid (48%)	For Zr and alloys of high content	F. M. Cain, *Zirconium and Zirconium Alloys* (*Amer. Soc. Metals*), **1953**, 176
Per litre : 100 g. ammonium fluoride 400 c.c. conc. nitric acid 200 c.c. fluosilicic acid Vol. made up with water	Rate of solution depends on temp.: 15 μ/min. at 24°C. 100 μ/min. at 46°C.	W. C. Schickner, J. G. Beach, and C. L. Faust, *J. Electrochem. Soc.*, 1953, **100**, 289
40–45 c.c. nitric acid 40–45 c.c. water 10 c.c. hydrofluoric acid	—	E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, 1954, **101**, 348 J. Belle and M. W. Mallett, *ibid.*, 339