ELECTROPOLISHING WITH SPECIAL REFERENCE TO TWO COMMERCIAL TYPES OF POLISHING APPARATUS FOR METALLOGRAPHIC PURPOSES

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With 8 figures

I.

In 1910 SPITALSKY (1) described, in a German patent then granted, an electrolytic process which imparted to silver a highly increased lustre in the course of a few minutes. This, according to the description of the process, constitutes the first known example of electrolytic polishing (electropolishing) that has come to the author's notice. The silver was placed as anode in an alkaline bath containing silver cyanide, and the current density was about 1 amp/dm^2—quite typical data.

The next twenty years saw the appearance from time to time of works touching more or less consciously on the idea of electropolishing, mostly in connection with electrolytic pickling or cleaning.

In 1930 the Société Le Matériel Téléphonique (2) was granted a French patent for electrolytic polishing methods for nickel, copper, aluminium and molybdenum. The method was developed by FIGOUR and JACQUET, and, for the latter, this work became the introduction to an important career of research in this field. Oddly enough, however, the patents remained almost unnoticed in spite of the fact that they contained all such elements as were essential to the later development. Not till 1935 did JACQUET really appear in the limelight with a work on electropolishing of copper in phosphoric acid solution (3), and, since then, a steadily increasing number of publications has appeared from all quarters and now totals more than 200 (4).

In the middle of the thirties the Battelle Memorial Institute and some American firms began a purely technical development, which has resulted in a number of industrially well-suited methods for metals (5). At the present time it is possible to electropolish 15 different metals and a number of alloys; of the alloys it holds good that a really brilliant lustre can only be achieved if they do not contain more than a single phase, as in the case of alfa brass or austenitic steel; polyphase alloys exhibit a more or less matt appearance, which is due to relief polishing caused by the different dissolving rates of the various phases.

No attempt should be made at making a too direct comparison between the appearance of a mechanically polished object and that of an electropolished. The special bright mirror finish which characterizes mechanically polished (short: mechanopolished) metals because of their quite plane surfaces cannot usually be achieved by means of electropolishing unless the object has previously been polished to almost the same brightness by mechanical means; this is due to the fact that electropolishing leaves the surface slightly wavy since scratches, etc. are only smoothed, not planed. But, on the other hand, electropolishing often imparts to metals an especially warm and beautiful lustre which cannot be achieved mechanically.

Often mechanopolishing covers up small impurities, porosities and other defects simply because a metallic film is applied to the place by the mechanical action. The polishing does not reach to the bottom. The electrolytic method polishes even submicroscopic unevennesses and uncovers all impurities. For this reason an electropolish will often appear less clean in the microscope than a mechanopolish.

It is especially important that electropolishing removes the uppermost layers of the surface; consequently the surface will possess no stresses and have no cold-worked

structure due to the grind. This is important to metallographists inasmuch as this affords a guarantee against false structure. In an electropolish pores, cracks and seams will appear enlarged due to edge corrosion, and evaluation of porosity, etc., should therefore be done with critisism.

The theory of electropolishing is not very exhaustive and much has been quite insufficiently elucidated. In the following a brief account of the present conception of the subject will be given.

The sample about to be electropolished is placed as anode in a suitable electrolyte (see later), and with the right choice of voltage and amperage a polishing action will take place. During this there forms on the anode surface a thin film of high viscosity and high electric resistivity, and in fact it is to this phenomenon that the polishing effect is due. The film will act in two ways. a) At the "ridges" (high points) of the surface it will be thinnest and the current density will accordingly be highest there. We must, of course, also consider the fact that the current density is always highest at edges, points and all kinds of projections. The dissolution of the metal consequently goes on at the highest rate from the ridges, and the surface will be levelled. However, this effect hardly extends down into the submicroscopic range. b) The film, which presumably contains various complex compounds of the anode metal, will exhibit very high concentration gradients with corresponding polarization differences; the concentration is highest at the bottom of the "valleys". The theory then is, that the metal is being passivated here either through oxydation of the surface or due to absorption of oxygen. This conforms with visual observations concerning the polishing action: this sets in at a minimum voltage v_1; at a somewhat higher voltage v_2 oxygen bubbles begin to develop on the anode surface. The best polish is obtained when the potential is slightly lower than v_2; in the first part of the interval v_1—v_2 the resulting polish will appear etched. As soon as visible development of oxygen occurs, corrosion will take place at those points of the surface, where oxygen bubbles stick to the film, and not till a further increase in potential causes the development of oxygen to be so vigorous that bubbles no longer are able to adhere to the surface, will a perfect polish again be obtained.

Agitation of the electrolyte plays an important part with regard to the thickness of the film, and consequently to the conditions of the polishing process. If no agitation whatever takes place, the anode should be placed horizontally below the cathode; such oxygen bubbles as may develop will then have a tendency to liberate themselves and rise; as the agitation is increased in intensity, the film formed will grow thinner, and the electrolysis voltage will drop.

The baths used for electropolishing can be classified according to the current densities they employ (4).

1) The first group works at room temperature and very low current densities, from 1 to 15 amp/dm². The surface must be quite finely ground beforehand, and the group is employed chiefly by metallographists. The voltage used varies between 2 and 40 volts.

This group may be divided into 3 sub groups.

a) Mixtures of perchloric acid and acetic acid, often with an admixture of acetic anhydride. The type was invented by JACQUET, and can be used for polishing Al, Fe, steel, Pb, Sn, U and a number of alloys.

Violent explosions have occurred with such baths, especially when industrially used; according to JACQUET however, an explosion hazard exists only if the perchloric acid concentration exceeds 50%, and by careless handling. A decided inconvenience in their use is their sharp pungent odour.

The polishing time is up to 15 minutes, usually 6—8.

b) Mixtures of phosphoric acid and water, sometimes plus alcohol or glycerol. These types also originates from JACQUET. Well suited for Cu, Zn, Cd, Mg, Co, rustless steels, brasses, etc. Polishing time usually 6—12 minutes.

c) Alkaline baths with alkali hydroxide or alkali cyanide; well suited for W, Cd, Zn, Ag, Au.

2) This group operates at current densities between 15 and 150 amp/dm², voltages between 15 and 60, and at an increased temperature which in industrial applications can be maintained by means of the heat produced by the current. The time required is 5 minutes or longer. The basis as a rule is phosphoric acid, sulphuric acid, chromic acid, citric acid, hydrofluoric acid with admixtures of various organic substances, e. g. wetting agents. The baths are used for Cu, Fe, Al, steel, brass, etc., and form the industrial group proper.

3) Group 3 operates at room temperature and very high current densities, from 200 up to as much as 3000 amp/dm² in extreme cases, and the voltage lies between 25 and 110. Times are very short, from $^1/_2$ second to 20 seconds.

The group may be divided into 2 sub groups.

a) Mixtures of perchloric acid with lower alcohols, possibly some glycerol and ethyl ether: especially well suited for Fe, Al, Zn, Pb, Ni, Ag, U, steel and a great number of metal alloys. The type was invented by DE SY and HAEMERS (6); a variant for polishing heterogeneous alloys, especially light metal alloys with a high silicium content has been developed by MATTE, JOFFE and DAVID (7); it gives reasonably good results with cast iron too.

b) Mixtures of nitric acid and methyl alcohol; well suited for Cu, Al, and alloys of these metals. This type was invented by H. E. BROWN (8); the strong nitric fumes are an inconvenience.

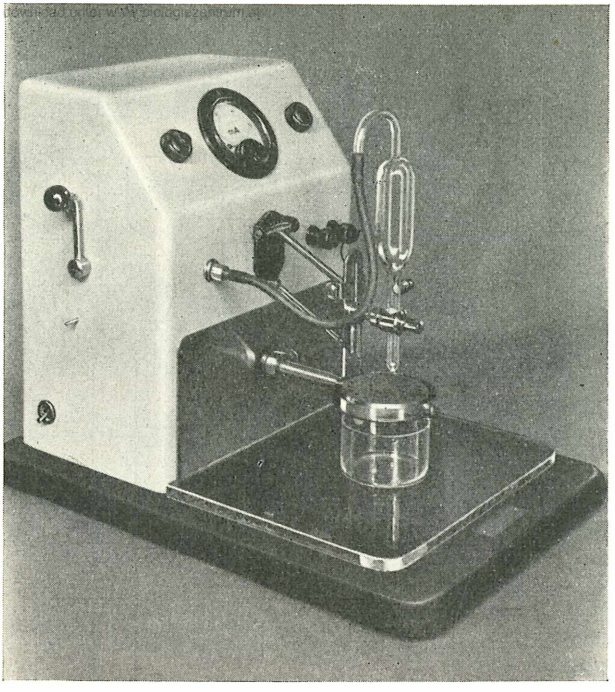
In spite of their composition, the perchloric acid-alcohol mixtures do not seem to involve any explosion hazard. The author has worked for many years with solutions of this type and has never even observed a decrepitation in spite of a great number of specially made experiments. However, a general warning should be made against evaporating the discarded solutions for the purpose of recovering alcohol or other substances; a content of 5—10% glycerol in the original solutions is believed to give safety also under these extreme circumstances, because glycerol is less volatile than all the other constituents.

Very rough surfaces can be polished with group 3; as a rule, however, initial grinding, corresponding to emery paper 0 is used. The methods are chiefly of metallographic interest, and have lead to the design and construction of some very rapidly acting and easily operated equipment, which greatly facilitates the daily work of the metallographist. This special development began at nearly the same time during the early years of the war in USA and Denmark (9) and was independently carried on, resulting in 4 different apparatus: the first to appear, the Danish Micropol, is specially designed for non-destructive structure examination, and the produced electropolish is a round spot with about 1 mm diameter; the apparatus is of the portable type and the electropolish can be made on any object regardless of its size and shape. To this apparatus there is no commercially available parallel made in other countries. The American Cenco and Buehler and the Danish Disa-electropolishers all have the same end in view, viz. the producing of a limited electropolish with a well-defined area ($^1/_2$—$1^1/_2$ cm²).

This similarity springs from the peculiar nature of the problems presented by a foolproof electropolishing method.

The optimum voltage and current density varies somewhat for the same material according to the size of the surface; the total amperage varies very much. This makes it very desirable always to use the same area; by the original methods described by JACQUET,

Fig. 1.
Micropol-electropolisher for non-destructive testing, testing on the spot, etc.



DE SY, etc., this is best done by using conform samples; with different surface areas, you must constantly change the electric conditions, and this requires practice and insight. There is an upper limit, moreover, for the areas that can be polished; group 3 for instance can usually only be employed for areas up to 2—3 cm^2, and even these sizes give a risk for blurred structures in places. For these reasons electropolishing have not been very extensively used in spite of the exceptionally sharp and well defined structures it provides, when rightly used.

Now there is another way out than using conform specimens; by placing the sample on a plate with an aperture, and only letting the electrolyte contact with the specimen through this, you will get an electropolish with the same size from case to case regardless of the shape of the sample, as long as the aperture is covered. This again assures uniform voltage and amperage from case to case. On this common principle the aforementioned Cenco, Buehler and Danish Disa electropolishers (and in a way the Micropol too) are built; yet the ways and means differ greatly in the different models; in the Disa-electropolisher several other conceptions have been included in the considerations before the final construction, as will be apparent from the later description.

II.

Fig. 1 shows the Micropol apparatus that appeared in 1942, fig. 2 gives the schematic diagram. The central part is an electrolysis pipette; the inside diameter of the point is about 1 mm. The pipette is filled with electrolyte (DE SY and HAEMERS) and placed so that the point rests on the specimen. The electrolyte is permitted to flow out slowly (in this way agitation during the polishing is provided), and the circuit is closed (0.1 amp). The duration of the process is controlled by means of a push button. The electropolish will appear below the point of the pipette as a round spot with about 1—$1^1/_2$ mm diameter. It is etched with nital in the usual manner.

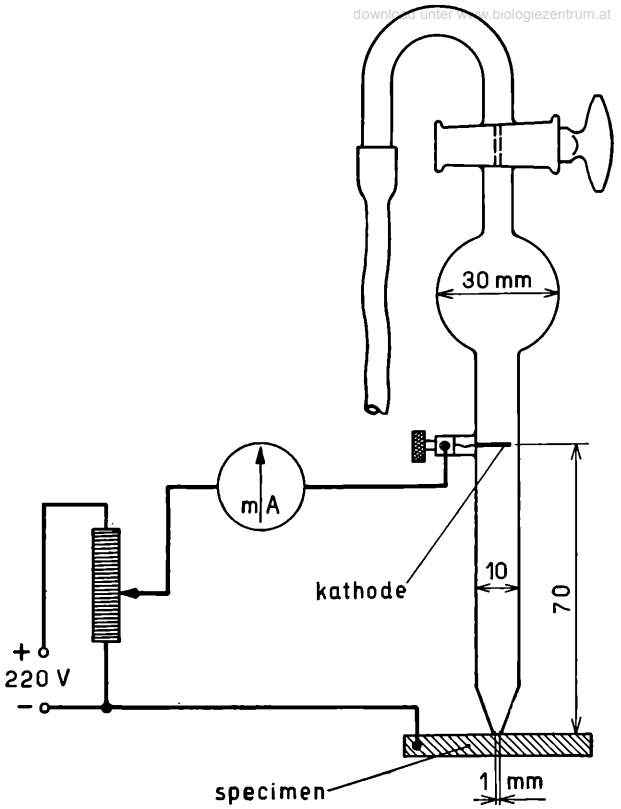


Fig. 2. Micropol principle.

In the case of high speed steel and cast iron, electrolysis is carried out for $^1/_2$ second, whereas 3 seconds will be required for most other steels. The quality of the electropolish compares favourably with that of any other type of set-up. The small surface of action leaves so slight a damage, that it is possible to employ the term "non-destructive testing". The author uses this electropolisher to check the hardening of the edges of finished tools after the grinding, for examining the structure of finished parts and of very large objects, that cannot easily be moved.

While this so-called "micropolishing" is sufficient for a number of purposes, especially most of the metallographic problems met with in an ordinary machine plant, it is in many cases, however, more desirable to polish larger surfaces since this permits forming a better impression of structural irregularities.

With the Micropol-principle as starting point the author constructed some more or less practicable set-ups and finally succeeded in making a model that solved the different problems in a satisfying way and was used for years in the laboratory the Dansk Industri Syndikat. It formed the basis for the now commercially available Disa-electropolisher, shown in fig. 3; the schematic diagram is shown in fig. 4.

The specimen about to be polished is placed face downwards on a horizontal plate (diaphragm) with the mentioned aperture. The plate which is interchangeable is placed as ceiling in an immovable electrolysis chamber. The specimen is fixed with a spring weighted electrode arm (anode). A pump conveys the solution to the electrolysis chamber, from which it escapes through the canal to the left and runs back to the electrolyte container. Liquid escaping through the aperture is conveyed back to the system by means of an overflow pan with drain pipe.

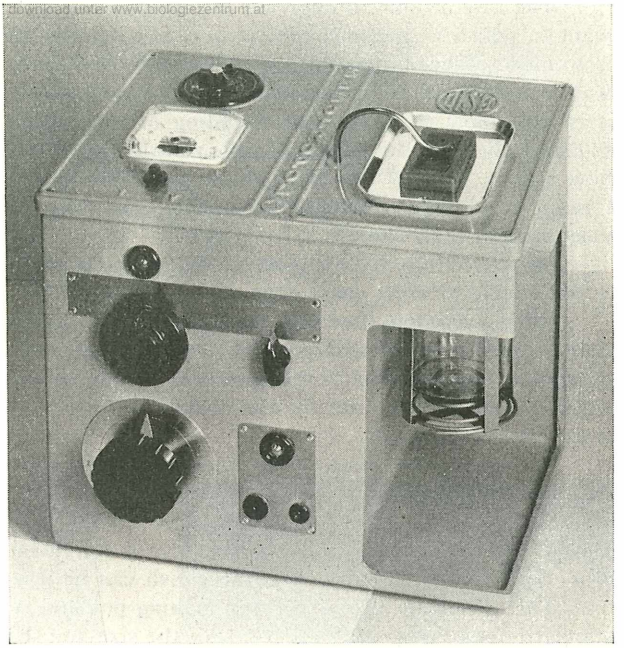
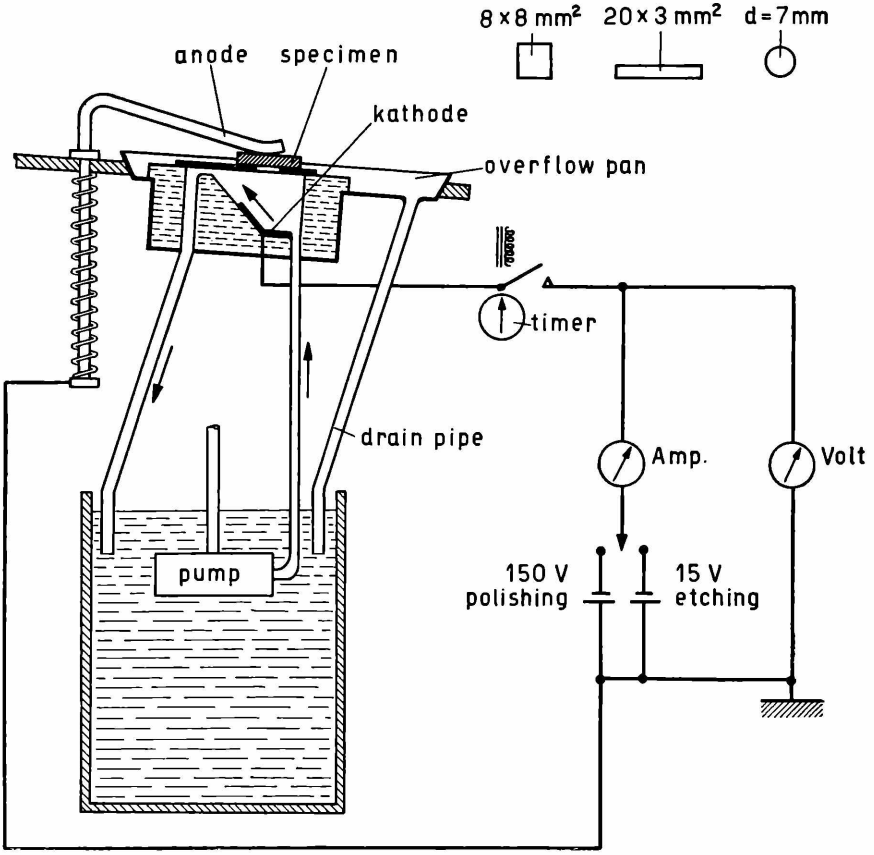


Fig. 3. Disa-electropolisher "foolproof" apparatus specially designed for quick routine work.

Fig. 4. Disa-electropolisher principle.



The rate of flow through the electrolysis chamber is controlled by a knob. If you want to polish a specimen that is not covering the aperture completely the flow rate is so much reduced, that the electrolyte only rises 2—4 mm above the opening. In this way it is possible to make passable edge examinations without embedding the piece; it is impossible to avoid some rounding oft the edges; by increasing the voltage and reducing the time this effect is somewhat lessened. A warning should be made: if the flow rate is reduced too much there is a risk of getting wavy lines on the surface foreign to the true structure, presumably caused by uneven flow on the surface of the visceous polishing film.

By embedding the test piece in Woods metal or the like before the electropolishing it is possible to make good edge examinations.

With maximum flow rate the agitation is violent and the cooling of the exposed surface intense; this enlarges the usual voltage and amperage limits and makes it possible to vary the size of the aperture—within reasonable bounds—without changing voltage, time or flow rate. It also makes the electropolisher very insensible to faulty or careless adjustment.

By varying the shape of the aperture it is possible to enlarge the applicability of the apparatus. As a rule it is sufficient to examine a representative micro section of a surface to get an adequate idea of the whole; a long narrow (rectangular) polish from the center of a round bar to the edge is for instance representative for the whole cross section; a similar rectangular polish can be used for the examination of welds.

The apparatus is powered for making polishes with an area of up to 1 cm^2; the standard diaphragms have apertures of the size and shape shown in fig. 4, upper corner right. The areas are $^1/_3$ or $^2/_3$ cm^2; all usual metallographic examinations can be effected by means of these standards.

The time of electrolysis is controlled by a timer, the voltage by a potentiometer knob (the big knob below left on fig. 3). A switch placed immediately above the potentiometer permits altering the voltage range from 0—150 volts to 0—15 volts or vice versa. The first range ist used for electropolishing, the second for etching. It is possible to etch most steels in direct continuance of the polishing (with the same electrolyte) by simply switching over to the etching range the last 2—4 seconds.

The meter measures either current or voltage by switching the contact directly below (fig. 3).

The glass beaker containing the electrolyte can be removed or set up in the course of a few seconds. It is fixed with a sort of bayonet lock. The internal pipe system keeps the electrolyte cool however much you use the apparatus.

The electropol is accompanied by a small auxiliary apparatus which permits electrolytic etching in a particularly simple manner with any type of electrolyte (fig. 5). The specimen is placed on the anode plate; a piece of cotton wool or felt is held with the tweezers and dipped into the electrolyte desired, after which the cotton wool is rubbed lightly against the place to be etched. The device can be connected to the electropolisher by means of a plug (fig. 3, lower corner right marked "etching"), and the usual etching voltage supply variable between 0 and 15 volts is used.

The electropolisher is powered with 110 or 220 a. c.

Fig. 6, 7 and 8 give examples of structures produced by means of the Disa-electropolisher. It is worth mentioning that the relief effect sometimes is greater in the electropolished structures than in the mechanopolished; this may be a drawback in the case of photographic reproduction by which it is incidentally strongly emphazised as compared with visual observation. In this latter case the author in nearly all cases considers the relief effect an advantage, since it greatly facilitates distinction between the different structural elements.

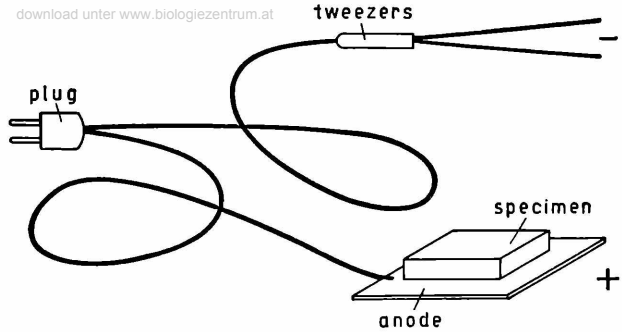


Fig. 5. Auxiliary electroetching equipment in connection with Disa-electropolisher.

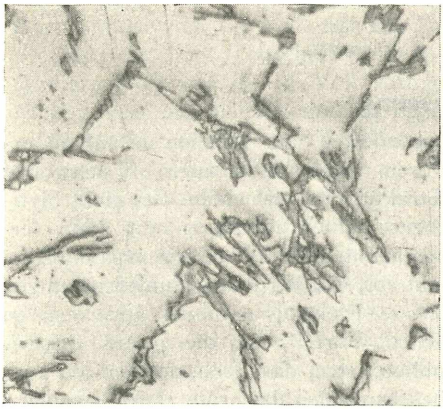


Fig. 6.

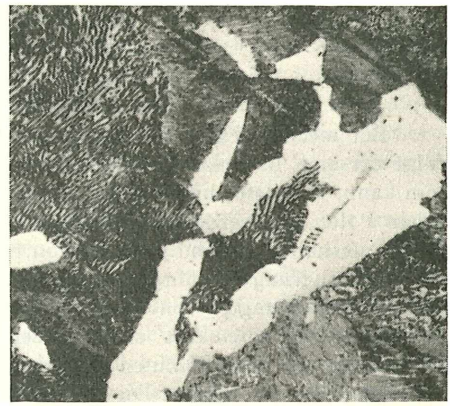


Fig. 7.

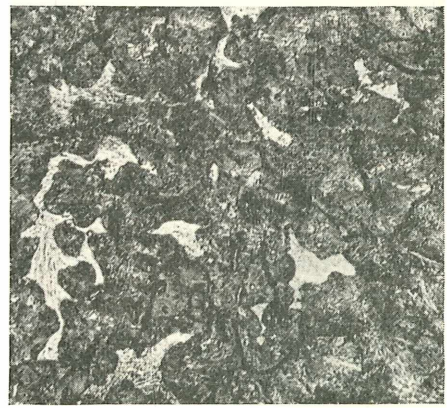


Fig. 8.

Fig. 6. Aluminium alloy with 0.15% Si, 1.28% Fe, 0.25% Mg, 10.00% Cu.
Polishing conditions: initial grind paper 0, 40 volts, 10 seconds. Unetched. 350 : 1.

Fig. 7. Siemens Martin carbon steel with 0.50% C, normalized.
Polishing conditions: initial grind 0, 40 volts, 10 seconds. Etching: switch 2 seconds. 620 : 1.

Fig. 8. Cast iron.
Polishing conditions: initial grind 00, 40 volts, 3 seconds. Etching: switch 1 1/2 seconds. 350 : 1.

Fig. 6 and 7 were made in the standard way that can be employed by nearly all steels and aluminium alloys (except those with high silicon content).

The electrolyte was made by mixing 2 parts of perchloric acid (d 1.20) with 7 parts of ethyl alcohol (96%) and 1 part of glycerol.

The aperture with 7 mm diameter was used.

Initial grinding with emery paper 0, 40 volts, 0.8 amp, 10 seconds. No. 6 is unetched, no. 7 was etched by switching over to the etching range for 2 seconds.

No. 8 was made by initial grinding to 00, 40 volts, 3 seconds. Etch $1^1/_2$ seconds. It is not always possible to electropolish cast iron (which by the way always appears more or less etched and with a black smudge that is wiped of).

When polishing aluminium alloys it is better to use an electrolyte without the glycerol, i. e. 1 part of perchloric acid and 4 parts of ethyl alcohol. This is also the best for very highly alloyed steels or mild steel[1]; the latter always gives some corrosion spots, easy to recognize however.

Heterogeneous aluminium alloys, especially with silicon, and cast iron sometimes are better polished with a solution containing

perchloric acid (d 1.61)	35 ml
methyl alcohol	840 ml
glycerol	125 ml

Brasses are best polished with a solution containing

nitric acid conc.	1 part
methyl alcohol	2 parts.

Zusammenfassung

Bei mechanischer Polierung, nicht zum mindesten von weichen Metallen, erfolgt oft eine Bedeckung von Unreinheiten, Poren u. ä., wie es auch oft schwierig sein kann, Kaltdeformation, das heißt falsche Struktur, zu vermeiden. Bei elektrolytischer Polierung werden die obersten Oberflächenschichten abgezogen, und man vermeidet deshalb vollständig Fehler von der oben genannten Art. Oberflächenspannungen, von der Polierung herrührend, kommen auch nicht vor, was bei Röntgenuntersuchungen und Härteprüfungen von Bedeutung ist. Gewisse Elektrolyte bieten außerdem in Beziehung auf die Zeit einen außerordentlichen Vorteil, da die ganze Schliffherstellung auf 1—2 Minuten von dem Augenblick, wenn das Grobschleifen anfängt, herabgesetzt werden kann. Die in dem Artikel beschriebenen Apparate zielen besonders darauf, diese letzten Methoden auszunutzen.

Abb. 1 und 2 zeigen einen Apparat, Micropol, der besonders für zerstörungsfreie Strukturuntersuchung und Untersuchung von unhandlichen Stücken bestimmt ist, da er Gegenstände polieren kann, ohne dieselben zu bewegen. Er besteht aus einer Elektrolysenpipette, deren Spitze ein Lumen von etwa 1 mm hat. Die Pipette wird mit Elektrolyt gefüllt und mit der Spitze auf dem Probestück ruhend, das als Anode fungiert, angebracht; man läßt die Flüssigkeit langsam hinauslaufen, und gleichzeitig wird der elektrische Strom (etwa 0,1 A) eingeschaltet. Die Elektrolysenzeit ist $^1/_2$—4 Sekunden. Unter der Spitze bildet sich ein elektropolierter Fleck, etwa 1 mm im Diameter; die Qualität ist auf der vollen Höhe anderer elektropolierter Oberflächen. Micropol kann die meisten der Aufgaben einer normalen Maschinenfabrik lösen.

Abb. 3 und 4 zeigen einen anderen Apparat, Disa-Elektropol, der im allgemeinen für metallographische Laboratorien bestimmt ist. Er bringt ebenfalls lokale Elektropolierungen, aber bis auf 1 cm² im Areal und mit jeder gewünschten Form hervor. Die Größe und Form des Probestückes ist ohne Bedeutung, wenn es nur auf dem Apparat angebracht werden kann. Es wird auf einer Platte mit einem Loch, dessen Größe und Form der fertigen Elektropolierung entsprechen werden, angebracht. Das

[1]) This electrolyte is in fact the better one for all-round purposes, but the recommended standard electrolyte has a longer life and is to be preferred in routine work. The diaphragms too last longer, when glycerol is present. An addition of 5% ethyl ether makes the polishing still brighter, but the ether evaporates quickly.

Festspannen geschieht mittels eines federbelasteten Anodenarmes. Die Platte bildet die Decke einer feststehenden Elektrolysenkammer mit Kathode unten und kann in ein paar Sekunden ersetzt werden. Beim Regulieren der Geschwindigkeit der abgebildeten Pumpe kann man die Geschwindigkeit der durchströmenden Flüssigkeit ändern; mit herabgesetzter Geschwindigkeit kann man Oberflächen elektropolieren, die nicht ganz das Loch decken, das heißt, daß Randuntersuchungen möglich sind. Nach vorherigem Einbetten in Woods Metal wird das Randuntersuchen noch besser.

Die Polierzeit wird auf einem Zeitschalter (in der Regel 15 Sekunden beim Vorschleifen auf Papier 0), die Spannung auf einem Potentiometer (in der Regel 40 Volt) eingestellt. Strom und Spannung können auf demselben Meßinstrument abgelesen werden.

Das polierte Gebiet ist normal $^1/_3$—$^2/_3$ cm^2; die Standardformen sind in Abb. 4 in der oberen rechten Ecke gezeigt. Innerhalb dieses Gebietes braucht man die elektrische Einstellung des Apparates nicht zu ändern, die übrigens innerhalb weiter Grenzen variieren kann, ohne das Resultat zu ändern.

Beim Ändern der Form des Loches kann man die Verwendbarkeit außerordentlich viel erweitern. Ein länglicher Schliff ist für Untersuchung von Schweißungen oder von einer Stange vom Kern bis auf den Rand geeignet.

Mittels eines Umschalters kann man das Spannungsgebiet von 0—150 Volt (Poliergebiet) auf 0—15 Volt (Ätzgebiet) und umgekehrt ändern. Polierung und Ätzung von den meisten niedrig legierten und unlegierten Stählen können dadurch vorgenommen werden, in 15 Sekunden zu polieren und dann in demselben Arbeitstakt mittels des Umschalters mit 2—4 Sekunden Ätzung abzuschließen. Beide Prozesse werden mit derselben Einstellung des Potentiometers vorgenommen.

Abb. 5 zeigt eine einfache Vorrichtung für elektrolytische Ätzung mit anderen Elektrolyten als den im Apparat vorkommenden. Mit der Pinzette, die als Kathode wirkt, nimmt man ein Stück Watte, das in die gewünschte Ätzflüssigkeit getaucht und über die polierte Oberfläche gestrichen wird. Das Probestück liegt auf einer Anodenplatte. Dadurch wird die Oberfläche in normaler Weise elektrolytisch geätzt.

Mit dem gewöhnlich verwendeten Standardelektrolyt kann man Fe, Al, Zn, Pb, Ag, Ni, fast alle Stahl- und viele Gußeisentypen, eine große Anzahl von Aluminiumlegierungen (bei hohem Gehalt von Si werden die Resultate nicht besonders gut), einige Kupferlegierungen u. a. polieren. Durch die Anwendung der Spezialelektrolyten kann das Gebiet erweitert werden. Im Artikel werden verschiedene Elektrolyte erwähnt.

Postscript

Since the above article was written the author have tried out a new type of electrolyte, a variant of DE SY and HAEMERS electrolyte:

perchloric acid (d 1,20)	2 parts
ethyl alcohol (96 %)	7 parts
butyl cellosolve (2-butoxyethanol)	1 part.

It seems to combine nearly all the good points in the different perchloric acid-alcohol mixtures, and even widens the alloy field covered by the others. As an electroetching agent it gives exceptionally well defined structures. It polishes and etches somewhat slower than the usual mixtures.

References

1. *Spitalsky,* Germ. Pat. Nr. 225873 (1910). — 2. *Figour H.* et *Jacquet P.,* Le Matériel Téléphonique. Brev. franç. No. 707526 (1930). — 3. *Jacquet P. A.,* Nature **135** (1935): 1076. — 4. A nearly complete list is presented by *P. A. Jacquet* in Metal Finishing, May and June 1949. — 5. *Pray* and *Faust,* Iron Age **145** (1940): 33. — 6. *de Sy* and *Haemers,* Stahl und Eisen **61** (1941): 185. — 7. *Jacquet P. A.,* Le polissage électrolytique des surface métalliques..., tome 1, 1948, p. 51. — 8. *Brown H. E.* (editorial), Met. Progress **36** (1939): 756. — 9. *Wayne Parcel,* Met. Progress **42** (1942): 209. — 10. *Knuth-Winterfeldt,* Kem. Maanedsblad 11 (1943). Metaux et Corrosion **23** (1948): 5.