

# Technology Section

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## EFFECT OF VISCOSITY OF ELECTROLYTE USED IN ANODIC DISSOLUTION AND ELECTROCHEMICAL MACHINING

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**Abstract.** These investigations are intended to study the effects of increase of viscosity of electrolyte on the various parameters involved in electrochemical machining. Some results obtained under static conditions of sodium chloride solution containing glycerol as viscosity improver have been obtained. Potentiostatic polarization curves obtained suggest that an increase in viscosity of solution resulted in a decrease of limiting current density on nickel. The surface finish of nickel specimens evaluated by Talysurf measurements showed that an improved surface finish is obtained by the use of glycerol in such solutions. The use of viscous solutions in electrochemical machining shall, however, need additional pumping requirements.

The high current densities involved in ECM require high flow rates during the process. The purpose of such high flow rates is to carry away the dissolved metal ions without greatly changing the local conditions in terms of conductivity, temperature and solubility. All these factors are in some way responsible for mass transfer at the electrode electrolyte interface.

Although some work has been reported on such mass transfer effects in electroplating, not enough literature is available pertaining to ECM conditions. The parameter of electrolytes used in ECM, such as viscosity, is not only important as regards the pumping requirements but it may as well effect the quality of the surface finish obtained. Applications of the Jacquet polishing curve to ECM has been emphasized.<sup>1</sup> The polished surface obtained in ECM, alongwith the machining, make the process more important than the conventional method of separate machining and polishing. In ECM, however, high pressures are needed to pump the electrolyte into the narrow electrode gap which demands the viscosity of the electrolyte be low. To achieve lower viscosities addition agents may be successfully employed,<sup>2</sup> provided they do not otherwise effect the ECM process. Since the thickness of the diffusion layer that prevails at the anode during the polishing plateau region is responsible for the kind of surface finish obtained, any factor such as flow rate or viscosity will affect the thickness of the diffusion layer and hence the type of surface finish obtained. The use of highly viscous substances, such as glycerol, have been suggested to increase the viscosity and conversely acetic anhydride or alcohol which lowers the effective concentration of solvating water molecules.<sup>3</sup> Therefore, to choose a suitable viscosity so as not to hamper much the pumping requirements, an addition of proper amount of glycerol may be advantageous.

The dissolved species reacting at the electrode under the static condition must be transported from the bulk solution toward the electrode or vice versa. This transport can take place: (a) by diffusion (caused by concentration differences in the solution); (b) by migration (movement of the ions under the influence of the electric field); and (c) by convection (due to the hydrodynamic flow of the liquid which drags alongwith the dissolved species).

Keeping in view the requirements of high flow rate in ECM and the extra pumping pressure to overcome the viscous forces it was considered useful to investigate the effects of glycerol additions under static conditions. Because of the nonavailability of an ECM cell having a sophisticated system of controlling the gap width of electrodes, it was felt that the effect of glycerol additions, such as limiting current density and surface finish, may not be noticeable. The continuous increase in gap width, with an ECM cell having no control for gap width would affect the velocity of the solution and, therefore, the current density and surface finish. Another reason for choosing the static conditions was the difficulty involved in defining the electrolyte velocity in mechanically stirred solution. All the experimental work reported in this paper was carried out under static flow conditions of flow rate and it was assumed that the results obtained could be applied in ECM after suitable modifications.

### Experimental

The electrolytic cell was made on a one-litre flat-bottomed glass beaker and the solutions were made of 10, 20 and 30% NaCl (w/v). The salt used was analytical grade. The solutions were discarded after each run. The glycerol (A.R.) The layout of the apparatus is shown in Fig. 1. The temperature of the solution was kept at  $20 \pm 1^\circ\text{C}$  and the pH was measured before and after the experiment.

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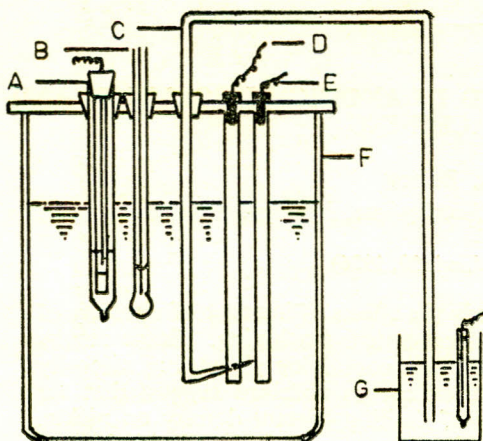


Fig. 1. Electrolytic cell for nickel under static flow condition.

The anodes were made in the form of rectangular bars in size of  $1.25 \times 1.25 \times 10$  cm of 99.9% pure nickel. The specimens were ground on different grades of emery paper and finally polished on a polishing wheel to get a surface finish of a few micron. A working area of  $0.25 \text{ cm}^2$  was exposed while the remaining area was lacomitted. The cathode was made of pure copper with a working area of  $0.25 \text{ cm}^2$ , i.e. the same as anode. The two electrodes were positioned and screwed at a perspex bar and the connections made with crocodile clips. The gap width of the two electrodes for each experiment was kept constant at a value of 1.5 cm. Too narrow gap width under static conditions of flow may result in local overheating of the solution and, therefore, a gap of 1.5 cm was thought to be proper.

A saturated calomel electrode with a luggin probe made of glass tube connected with a polythene tube, was used. The saturated calomel electrode was standardised periodically and all the results presented are referred to saturated calomel electrode as the standard electrode.

All the polarization curves were obtained when the anode potential was controlled by a potentiostat of the type Amel 555 (accuracy of working electrode  $\pm 0.1 \text{ mV/V}$ ;  $\pm 2 \text{ mV/A}$ ; delay time  $100 \mu\text{sec}$ ; maximum current load 10A). A scanning rate of 0.5 volt/5 min was used and the current was measured by an ammeter at the end of 5 min. Duplicate experiments were performed to check the reproducibility of the results. All the experimental variables such as gap width, static flow condition and temperature of the electrolyte were kept constant and only the composition of the solution was changed to study the effect of increase in anion concentration and glycerol additions.

The surface finish was examined at different anode potentials with a Reichart microscope and only a detailed study was conducted in 20% sodium chloride solution which was used as a base solution in glycerol additions. The comparison of surface smoothness was recorded by Talysurf machine with a magnifica-

tion of 20 and 2,000 times horizontal and longitudinal, respectively.

Although there are a number of methods available<sup>4</sup> for the measurement of viscosity of liquids, Ostwald's viscometer was used, due to its simplicity, for the determination of viscosity of solutions.

## Results

*Electropolishing of Nickel in Sodium Chloride Solutions.* The different polarization curves obtained in 10, 20 and 30% sodium chloride solution are shown in Fig. 2. All the curves obtained consist of five distinct regions, i.e. AB, BC, CD, DE and EF. The part AB was the region where metal dissolved crystallographically but numerous small pits also appeared on the surface and form of the curve was typical of activation controlled reactions. Over the region BC a thin black scaly film appeared on the surface which gradually thickened till the point C was reached and the rate of growth of the film seemed to be dependent on the rate of increase of anode potential. In the region CD, the film gradually became thinner and finally peeled off the surface. The breakdown of the film appeared to be both electrochemical and mechanical. The surface underneath the scaly film was pitted and rough. During the region DE, the surface became polished. The current density remained constant and the surface was covered by a viscous diffusion layer which could be seen falling down as light green viscous liquid. When the anode potential was increased to a value more than about 2.4, i.e. the part EF of the curves, the current density showed a gradual increase. The increase in current density was probably due to two factors in this region. Firstly, the oxygen evolution took place over the anode and part of the current was consumed in oxidation of the solution; secondly, the surface became pitted and thus resulted in the increase in surface area which caused an increase in the current density.

A detailed examination of nickel specimen was made in 20% sodium chloride solution and the micro-

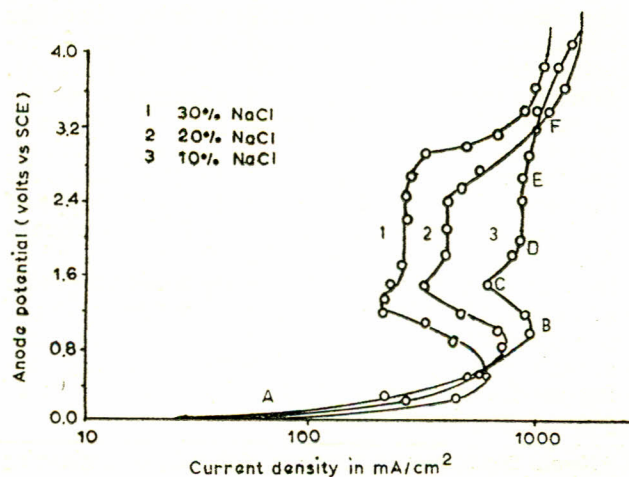


Fig. 2. Anodic polarization of nickel in sodium chloride solutions under static conditions,

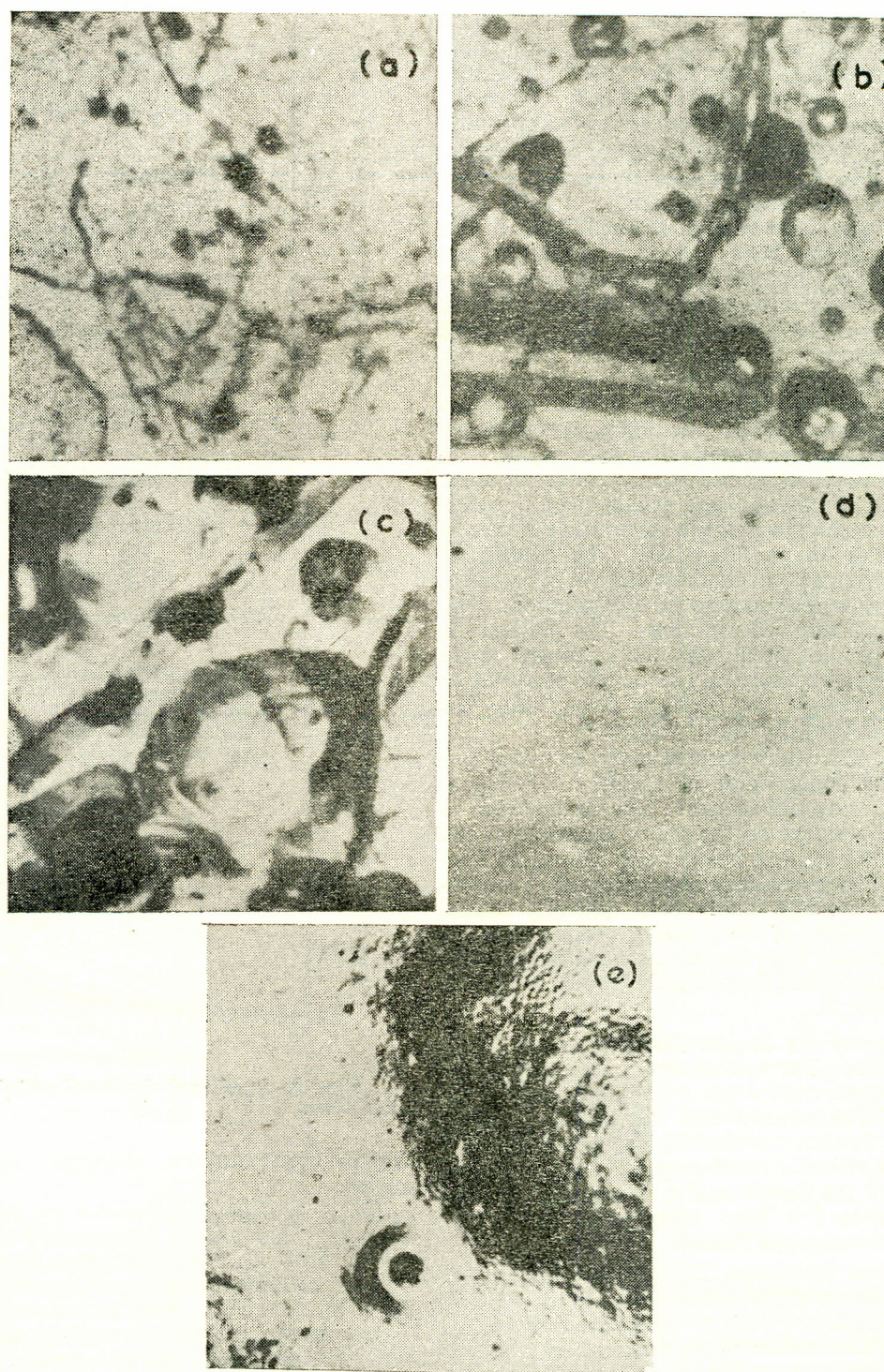


Fig. 3.

Micrograph	Polarizing potential (SCE)	Components
(a)	-0.04V	etched and pitted
(b)	+0.053V	heavily pitted surface
(c)	+0.100 V	increase in size of pits
(d)	+2.0 V	polished surface
(e)	+2.6 V	polished and pitted surface

graphs were recorded at different anode potentials which are shown in Fig. 3. At an anode potential less than  $-47$  mV, the surface was crystallographically etched, but also showed small round pits. When the anode potential was raised further the number and size of pits increased and this happened in the region of  $-47$  to  $+100$  mV. The surface became heavily pitted at above an anode potential of  $+100$  mV. The surface gradually became covered with a thin scaly film,  $\text{Ni}(\text{OH})_2$ ,  $\text{NiCl}_2$ . Such a formation and thickening of the film took place between 0.5 to about 1.4 and 1.7V. The electropolishing took place after the film dissolved gradually or peeled off after becoming thin over an anode potential of about 1.7V. Breakdown of the film occurred through the random formation of pits both at grain boundaries and within the grains and polishing arose through the bright pits coalescing and spreading locally covering the whole surface. It was found that pit formation was dependent on time, concentration of solution and potential of the electrode. No attempt was made to find the effects of other variables on pit formation. The number of pits at a given anode potential was more in 20 and 30% sodium chloride solution than in 10% solution. The number of pits increased with time. The size and the number of pits increased with the increased anode potential. Fig. 4 represents the anode potential vs anion concentration and surface finish, after the theoretical idea put forward by Hoar.<sup>5</sup>

The black film which formed over the nickel surface had the composition of  $\text{Ni}(\text{OH})_2$ ,  $\text{NiCl}_2$  as analysed by x-ray diffraction.<sup>7</sup> The composition of the film is dependent on the pH of the solution and since the pH of solution was between 5.6 and 10.5 before and after the experiment respectively, the composition in such a range should be a sparingly soluble salt.<sup>6</sup> The values of the limiting current densities showed a decrease when the anion concentration of the solution was increased from 10 to 30% sodium chloride solution (Table 1).

**Comparison of the Surface Finish Obtained in Different Solutions.** The surface finish examined in the polishing plateau regions was found dependent on the viscosity of the solution and the anode potential. The surface finishes recorded by Talysurf machine in 20% sodium chloride containing 2, 5, 10, 16, 20 and 30% glycerol are shown in Fig. 6 and Fig. 7. The surface texture has been represented as C.L.A. (central line average) in Table 3.

In solutions containing 2% glycerol the surface finish could be compared to the surface finish obtained in sodium chloride, while in all other cases the surface was rough. The surface finish obtained in 2% glycerol addition was smoother than the surface obtained in 20% sodium chloride without glycerol, which was obviously due to the greater viscosity of the former. The viscosities of different solutions are shown in Table 4.

Thus, the addition of glycerol was useful only to an extent of 2%. However, it seems probable that if the flow condition of the electrolyte was improved a

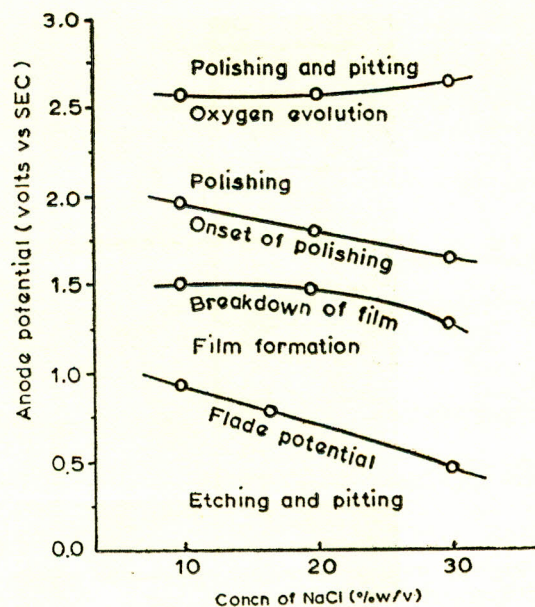


Fig. 4. Anodic potential vs anion

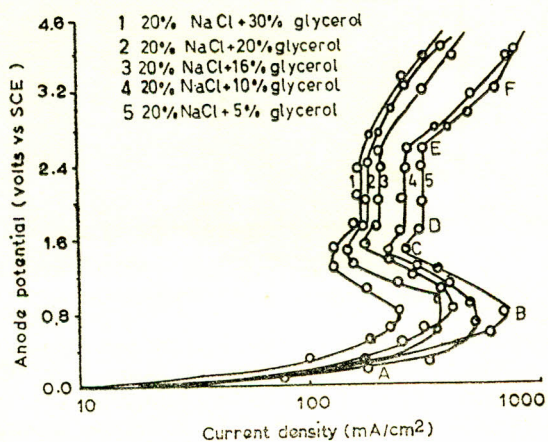


Fig. 5 Anodic polarization of nickel under static flow conditions.

slightly higher amount of glycerol might equally be useful.

**Effect of Glycerol Addition on Limiting Current Density.** The anodic polarization curves obtained with 2, 5, 10, 16, 20 and 30% glycerol addition in 20% sodium chloride solution are shown in Fig. 5. The form of curves was more or less the same. All the curves showed five distinct regions AB, BC, CD, DE, EF. In the region AB, the surface showed etched surface with small pits, while in the region BC, the current density decreased and the surface became covered with a black film which rapidly thickened. In the region CD, the film gradually dissolved and finally peeled off at and above an anode potential of 1.6. During the region DE, the surface was covered with a viscous diffusion layer and became pitted while in the region EF, the surface showed polishing. The

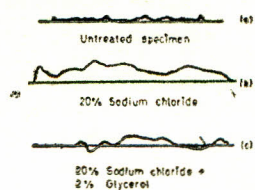


Fig. 6. Talysurf recordings on electropolished (Ni) in different solutions.

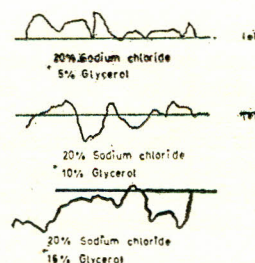


Fig. 7. Talysurf recordings on nickel electropolished in different solutions.

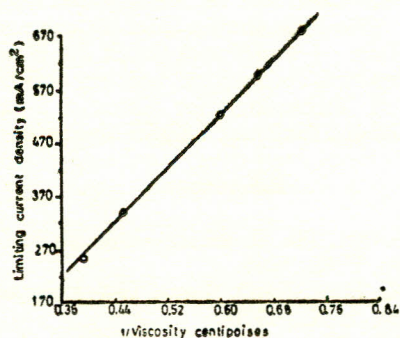


Fig. 8. Limiting current density vs 1/viscosity.

limiting current density decreased as the amount of glycerol addition was increased from 2 to 30%. The surface finish in solutions containing 2% glycerol was satisfactory while in the remaining solutions it was uneven polishing. The limiting current densities in various concentrations of glycerol is shown in Table 2.

**Discussion**

The polarization curves comprise distinct ranges of anode potential and the surface of anode varied in each region. The general pattern of the curves in case of sodium chloride solution and sodium chloride containing glycerol is the same which suggests that glycerol addition did not effect the electrode kinetics. The etched surface was obtained in the activation controlled region where the current density is a function of anode potential. The formation of scaly film below the polishing regions on the anode in all concentrations of glycerol of sodium chloride suggest that the chloride ion concentration did not effect its formation. The composition of such films when analysed was found to be Ni(OH)<sub>2</sub>NiCl<sub>2</sub><sup>7</sup> such a film is fairly conductive to ions as the current density

TABLE 1. INFLUENCE OF CONCENTRATION OF SODIUM CHLORIDE ON THE LIMITING CURRENT DENSITY.

Concn. % (w/v)	10	20	30
Limiting current density mA/cm <sup>2</sup>	840	400	250

TABLE 2. INFLUENCE OF GLYCEROL ADDITION TO 20% SODIUM CHLORIDE ON LIMITING CURRENT DENSITY.

% glycerol addition (w/v)	2	5	10	16	20	30
Limiting current density mA/cm <sup>2</sup>	375	330	270	210	180	170

TABLE 3. CENTRAL LINE AVERAGE (C.L.A.) IN MICROINCHES.

Figs. No.	7a	7b	7c	6a	6b	6c
C.L.A.	80.027	70.25	152.58	5	7.69	11.38
						3158

TABLE 4. EFFECT OF GLYCEROL ADDITION TO 20% SODIUM CHLORIDE SOLUTION ON VISCOSITY.

addition of glycerol	0	2	5	10	16	20	30
Viscosity Ns/m <sup>2</sup> 10 <sup>-3</sup>	1.20	1.26	1.36	1.62	2.24	2.39	3.60

did not fall below 230 mA/cm<sup>2</sup>. The peeling of the film at higher anode potentials seems to be both electrochemical and mechanical. The mechanical breakdown of such film is further supported by the evidence that increased flow rates resulted in breakdown of the film at lower anode potentials<sup>7</sup>.

The limiting current densities obtained in different chloride ion concentrations suggest that current density decreased with the increase in anion concentration. The explanation for such a decrease is, however, not very clear. The results obtained by Higgins<sup>(8)</sup> on electropolishing of nickel in hydrochloric acid showed a decrease in limiting current density from 2.37 A/cm<sup>2</sup> to 0.071A/cm<sup>2</sup> when the concentration of electrolyte was increased from 2 to 10 M solution. A similar decrease was found by Hoar and Rothwell<sup>9</sup> on copper, when electropolished in phosphoric acid and the concentration was increased from 0.1 to 7 M solution. The explanation given by Hoar for such a decrease in limiting current density is an increase of solution resistance within the pores of the loose layer of corrosion product in the case of more concentrated solution.

The distinct region of limiting current density during which a smooth polished surface was obtained is due to the suppression of etching by the formation of a compact solid film on the anode as proposed by Hoar.<sup>6</sup> No attempt was made to analyse the composition of such a film in the present investigations. The chemical composition of the diffusion layer extracted and examined in the previous work<sup>10</sup> suggest that the accumulation of respective salt of nickel may

result in the precipitation at the anode surface. Therefore there is more probability of the respective salt being the composition of the film rather than the oxide. However, some further analysis of the solid film of the anode is needed to confirm such a suggestion.

When a graph was plotted between the limiting current density and the inverse of viscosity (Fig. 8) almost a linear plot was obtained which suggests that viscosity of the solution affects the mass transfer across the diffusion layer substantially. The 'limiting' current density suggests that the process is diffusion controlled. Moreover, the thickness of the diffusion layer is decreased<sup>11</sup> by the increase in viscosity of the solution which result in the smoothening of the smaller convexities and a better surface finish is obtained. This is proved by the Talysurf measurement in the present investigation. The surface obtained in sodium chloride, containing 2% glycerol, was better than in sodium chloride solution containing no glycerol. The reason for improvement in surface finish by an addition of 2% glycerol only and not in other solutions is not clear. Probably the poor surface finish obtained in case of glycerol additions by more than 2% is due to the poor mass transfer rates prevailing at the electrode. The higher viscosities of the electrolytes result in lower current densities and therefore, the mass transfer mechanism is decreased both by diffusion and electric migration. Such a decreased mass transfer rate results in the precipitation of the dissolved species in the near vicinity of the electrode and, therefore blocks the metal surface for fresh electrolytic dissolution.

The present investigations suggest that a limited improvement in surface finish can be achieved by the increase in viscosity of the electrolytes under the static flow conditions. However, the higher flow rates needed for ECM to achieve higher current densities and machining efficiencies, would need high pumping requirements if any increase in viscosity of the electrolyte is made. Thus, for a typical electrolyte (20% sodium chloride) with a viscosity of  $1.2 \times 10^{-3}$  Ns/m<sup>2</sup>★ the minimum pressure required to overcome viscous forces alone in the case of flow between parallel plates separated by a distance of 0.125 mm at a velocity of 3000 cm S<sup>-1</sup> is  $2.7 \times 10^5$  Ns/m<sup>2</sup> per centimeter of the channel. The calculations are based on the following formula<sup>12</sup> which is derived from Hagen Poiseuille law.<sup>13</sup>

$$pv = 12nvx/Y^2$$

where  $pv$ , pressure difference required;  $n$  viscosity;  $v$  average flow velocity;  $x$  length of channel; and  $Y$  gap width

By comparison in electrolytes having viscosities of

1.365 and Ns/m<sup>2</sup> and 2.394 Ns/m<sup>2</sup> in case of 20% sodium chloride containing 5 and 20% glycerol respectively the pressures required to overcome the viscous forces would be  $3.08 \times 10^5$  Ns/m<sup>2</sup> and  $5.1 \times 10^5$  Ns/m<sup>2</sup> per centimeter of the channel respectively. Therefore, the increase in viscosity of the electrolyte would have a significant effect on the pumping pressure requirements.

### Conclusion

It has been shown that common salts such as sodium chloride can be used with limited success for electrochemical machining and electropolishing. Small increase in viscosity by glycerol additions shall generally result in an improved surface finish and a decrease in limited current density. Increase in viscosity of electrolytes in electrochemical machining shall, however, need additional pumping requirements.

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★One cP= $10^{-3}$  Ns/m<sup>2</sup> where Ns/m<sup>2</sup> stands for units of viscosity in the International System of Units.