

THE IMPORTANCE OF THE ELECTROLYTE IN ELECTROCHEMICAL MACHINING

M.A.LABODA, J.P.HOARE and S.E.BEACOM

*Research Laboratories,
General Motors Corporation, Warren, Michigan, USA*

Received May 5th, 1970

Steel tube cathodes were investigated in an electrolytic grinding test rig in solutions of NaCl, NaClO₃, and Na₂Cr₂O₇ as a function of concentration and potential. Solutions of NaClO₃ gave superior results with respect to surface finish and dimensional control at high metal removal rates. No electrochemical machining (ECM) was observed in Na₂Cr₂O₇ electrolytes. From data obtained on soft iron microelectrodes using potentiostatic polarization and galvanostatic stripping techniques, the ECM behavior observed for the machining of steel in the three electrolytes was accounted for in terms of the buildup and breakdown of protective films on the steel surface.

In the simplest terms electrochemical machining can be described as a machining system in which metal is removed electrochemically from the anode of an electrolytic cell; the cell is so arranged electrically and mechanically as to promote a continuous, economical process. While the impact of electrochemical machining on the international scene has not been great, it is obvious that it soon will become a subject of interest. This observation is based upon the use of ECM in the United States, in several European nations, and in Japan.

ECM has found its greatest use to date in the aerospace industries in the form of large, so-called "plunge" cutting machines^{1,2} which cut very intricate shapes in difficult-to-machine, hightemperature alloys. At the same time, it was recognized that there were other forms of the ECM cell such as the electrolytic grinding, deburring, and honing machines.

In attempting to apply ECM machines employing NaCl based electrolytes to everyday operations in the automotive industry, a number of persistent difficulties were encountered. It was found that the majority of steels normally used did not lend themselves to the ECM operation. In most applications under consideration, dimensions could not be held, tolerances could not be met, surface finishes were not satisfactory, and because of unwanted cutting at some distance from the cathode, "stray" cutting, the ECM operation could not be made compatible with other manufacturing operations. In addition, because of the "stray" cutting, the workpiece integrity was destroyed.

Despite development work by various groups throughout the world, the problems persisted. Recently, work carried out at the General Motors Research Laboratories indicated the significance of the electrolyte used in ECM. Of several hundred electro-

lyte combinations studied, the work described in this paper gives experimental evidence to substantiate the conclusion that sodium chlorate is a superior ECM electrolyte, especially for hardened steels. Comparisons of physical results in surface finish, metal removal, and "stray" cutting under various conditions on the same steel were carried out. In an effort to explain the observed ECM behavior of these electrolytes, basic studies of the buildup and breakdown of oxide films formed on iron surfaces were undertaken consisting of the analysis of polarization and constant current stripping curves.

HISTORICAL BACKGROUND

A number of years ago, the Electrochemistry Department of the General Motors Research Laboratories became interested in finding a better operating electrolyte for ECM machines. Initial studies were concerned with determining the controlling parameters of the process using the generally employed electrolyte, NaCl.

A sketch of the first type of cell used in these studies is presented in Fig. 1. The cell was constructed from a nylon cylinder which was machined in two halves such that a solution gap of about 0.025 cm was maintained when the halves were clamped together. As shown in the sketch, a copper cathode was held in position on one side of the gap; and the steel anode to be machined was held in position on the opposite side of the gap. The NaCl solution was pumped through the gap, and the electrodes were connected to a rectifier. A small gap space was required so that high currents (60 to 200 A/cm²) could be passed to give a high metal removal rate. As the steel anode dissolved, the small gap between anode and cathode could not be maintained so that the gap space had to be adjusted manually by the thumb screw attached to the steel anode.

Data were obtained to evaluate current-potential relationships, metal removal rates, and solution temperature effects as a function of the electrolyte concentration. Although satisfactory metal removal rates (0.107 cm/min of tool steel H-13 at 132 A/cm² in 30% by wt of NaCl) and good surface finishes ($5 \cdot 10^{-4}$ cm) were obtained, dimensional control was poor in all cases due to the "wild cutting" by stray currents.

The next approach was designed to find an additive for the NaCl electrolyte to provide a selective inhibition of the metal surface along the sides of the cut. In this way, the action of stray currents beyond the cutting face of the tool cathode would be suppressed and wild cutting could be eliminated. An extensive range of inorganic and organic addition agents including acids and their sodium salts, alcohols, amines, thiols, and aldehydes were added to NaCl electrolytes over a wide concentration range. These experiments were carried out in the electrochemical grinding test rig shown in Fig. 2* and described in the Experimental section of this report. Steel tubes

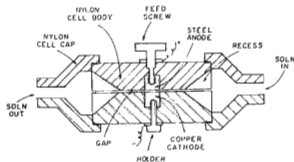


FIG. 1
Sketch of Cross Section of the Nylon Cell

* See insert facing p. 688.

M.A.LABODA, J.P.HOARE and S.E.BEACOM:
Importance of the Electrolyte in Electrochemical Machining

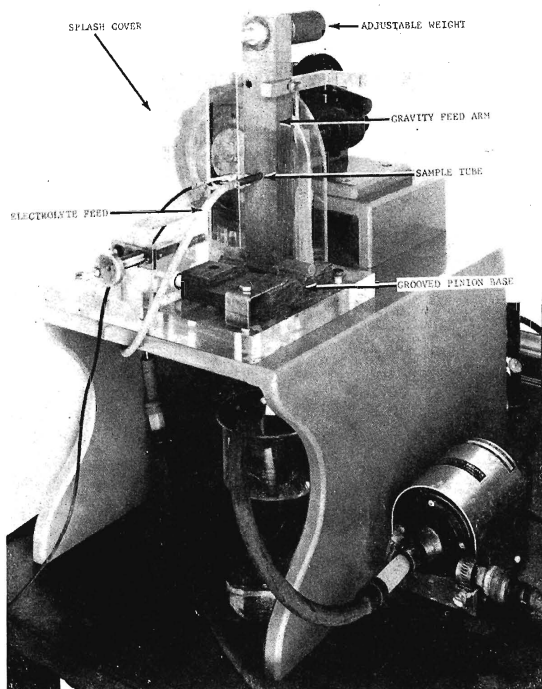


FIG. 2
Electrochemical Grinding Test Rig

served as the anodes, and the ends of these tubes were electrochemically machined at the face of the diamond-studded bronze wheel. The effectiveness of the electrolyte was evaluated in terms of the metal removal rate, squareness of the cut, and surface finish.

From the results of this work, it was concluded that for the most part a commercially satisfactory ECM electrolyte giving good dimensional control was not to be found with NaCl based electrolytes. Either the additives did not impart selective inhibition characteristics to the electrolyte, or had poor conductivity, or were prohibitively expensive. The results of other investigations^{3,4} along these lines seem to support this conclusion.

Since the ECM system is an anodic corrosion process, the electrolyte cannot be considered merely as a conducting medium of the ECM machine as it is by many authors in the literature in theoretical analyses of this system. One must take into account the electrochemical properties of a given electrolyte in contact with a given metal or alloy if significant progress is to be made. With this viewpoint in mind, an intensive search of available materials was carried out at the General Motors Research Laboratories to find a satisfactory ECM solution giving good metal removal rates with acceptable surface finish and the desired dimensional control.

Out of these screening efforts, the best electrolyte was found⁵ to be a solution of NaClO₃. The results of the machining of steel tube ends as a function of the nature of the electrolyte, the concentration of the electrolyte, and the potential give dramatic testimony to the importance of the electrolyte in a given ECM operation. These data are presented in this report.

EXPERIMENTAL

Electrochemical machining of 1020-steel tubes was carried out in the laboratory electrolytic grinding device of Fig. 2*. The tube was held with an adjustable weight against the face of a high-torque, rotating, bronze-sintered, diamond-impregnated wheel. Previous back-etching of the wheel face allowed the diamonds to protrude from the surface so that a gap space of 0.0025 cm could be maintained. By pumping the solution through the tube anode, a jet of electrolyte was directed against the face of the grinding wheel cathode in such a manner that uniform flow of the solution was obtained over the end of the tubes. The entire cutting assembly was enclosed in a plastic box so that the electrolyte draining from the box could be returned to the reservoir. At a preselected applied potential, the observed current was allowed to flow for one minute. The sample tube length was measured before and after ECM with a micrometer to determine the metal removal rate, and the ends tube were examined under a microscope of 25× power to assess the wild cutting and the surface finish. Solutions of NaCl, Na₂Cr₂O₇ and NaClO₃ at various concentrations were investigated.

In an effort to explain the observed behavior of the electrolytes, polarization curves and constant current stripping experiments were made on soft iron beads (~0.04 cm² in area) melted at the end of iron wires. After holding the beads in a reducing flame of a burning hydrogen jet to reduce any oxides, they were imbedded in polyethylene so that only the hemisphere of the bead was exposed to the electrolyte. Teflon spaghetti was used to cover the wire lead, and the electrode was mounted in one side of a Teflon cell⁶ filled with the proper electrolyte. A saturated calomel electrode (s.c.e.) was placed in the other side of the cell. With O₂ bubbling through the solution, the potential held by a 61 R Wenking potentiostat was increased stepwise after the steady-state current was recorded at each step with a 600 A Keithley electrometer. After the steady-state current was recorded, the potentiostat was disconnected by a mechanical switch and a constant

* See insert facing p. 688.

current cathodic pulse was applied with a Hg-wetted relay⁷ to the electrodes at each potential setting. From the trace obtained on a 541 Tektronix oscilloscope, the amount of oxide film was determined⁸ for each value of the potential. Only the apparent surface area was used in the calculation of the film thickness because the alternate formation and stripping of the film made the determination of a true area impossible.

RESULTS

Metal removal rates along with assessments of surface finish and degree of stray cutting are presented in Tables I to III for 1 020 steel in NaCl, NaClO₃, and Na₂Cr₂O₇, respectively, as a function of applied voltage. In each case, data were obtained at 50 and 250 g/l, and the mechanical machining component (operation without applied potential) was recorded. Evidently, mechanical machining contributes a very small amount to the total metal removed during ECM operation. In Fig. 3* is shown the photomicrograph of the steel tube end (0.635 cm OD with 0.089 cm wall thickness) before being machined. The appearance of the tube ends in each of the three electrolytes is given in the photomicrographs of Fig. 4* after one minute of ECM at an

TABLE I
ECM of 1020-Steel Tube Ends in NaCl

Closed circuit voltage V	Length before ECM cm	Length after ECM cm	Metal removal cm	Surface finish	Stray cutting	Remarks
At 50 g/l						
10	4.816	4.628	0.188	good	fair	
15	4.831	4.641	0.190	fair	poor	
20	4.884	4.684	0.200	no good	no good	heavy sparking
25	4.823	—	—	—	—	could not run test
Mechanical component	4.817	4.816	0.001			
At 250 g/l						
10	4.671	4.463	0.208	fair	poor	
15	4.940	4.762	0.178	poor	poor	
20	4.585	4.381	0.204	poor	poor	
25	4.447	4.216	0.231	no good	no good	heavy sparking
30	4.635	—	—	—	—	could not run test
Mechanical component	4.817	4.816	0.001			

* See insert facing p. 688.

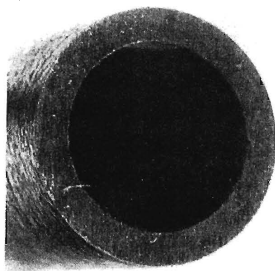
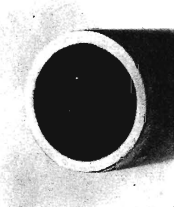
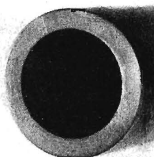


FIG. 3
Photomicrograph (25 \times power) of 1020-Steel
Tube End (0.635 cm OD with 0.089 cm Wall
Thickness) before ECM

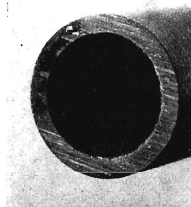
(A) NaCl 50 g/l



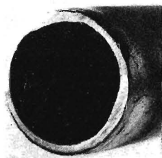
(B) NaClO₃ 50 g/l



(C) Na₂Cr₂O₇ 50 g/l



(D) NaCl 250 g/l



(E) NaClO₃ 250 g/l



(F) Na₂Cr₂O₇ 250 g/l

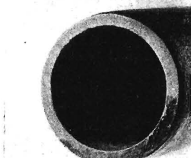


FIG. 4
Photomicrographs of Tube Ends after 1 min of ECM
Solution flow rate of 0.085 l/min for two concentrations, 50 g/l A, B, C and 250 g/l D, E, F, of
NaCl A, D, NaClO₃ B, E and Na₂Cr₂O₇ (C, F at an applied voltage of 10 V).

electrolyte flow rate of 0.085 l/min and an applied potential of 10 V. Under the same conditions, the photomicrographs of steel tube ends in NaCl and NaClO₃ at 20 V and in Na₂Cr₂O₇ at 30 V are displayed in Fig. 5*.

Figure 6 contains the steady-state polarization curves obtained potentiostatically on soft iron in the higher concentrations of NaCl (triangles), NaClO₃ (circles), and Na₂Cr₂O₇ (inverted triangles) in Fig. 6a, and the amount of charge, Q, in Fig. 6b in mC/cm² determined from the film stripping studies for the corresponding points shown in the polarization curves. It is to be noted that the potentials are recorded here with respect to a reference electrode and are not the cell potentials usually reported in ECM operation.

DISCUSSION

From an examination of the tables, it appears that the metal removal rate is independent of concentration when NaCl is used as the electrolyte, but is dependent on co-

TABLE II
ECM of 1020-Steel Tube Ends in Na₂Cr₂O₇

Closed circuit voltage V	Length before ECM cm	Length after ECM cm	Metal removal cm	Surface finish	Stray cutting	Remarks
At 50 g/l						
10	4.918	4.915	0.003	—	—	no ECM
15	4.914	4.912	0.002	—	—	no ECM
20	5.038	5.036	0.002	—	—	no ECM
25	4.754	4.743	0.011	no good	—	heavy sparking; some EDM
30	4.982	4.955	0.027	no good	—	heavy sparking; some EDM
Mechanical component	4.760	4.757	0.003			
At 250 g/l						
10	4.808	4.804	0.004	—	—	no ECM
15	4.912	4.907	0.005	—	—	no ECM
20	4.803	4.797	0.006	—	—	no ECM
25	4.911	4.907	0.007	no good	—	heavy sparking with EDM
30	4.835	4.793	0.042	no good	—	heavy sparking with EDM
Mechanical component	4.915	4.914	0.001			

* See insert facing p. 688.

M.A.LABODA, J.P.HOARE and S.E.BEACOM:
Importance of the Electrolyte in Electrochemical Machining

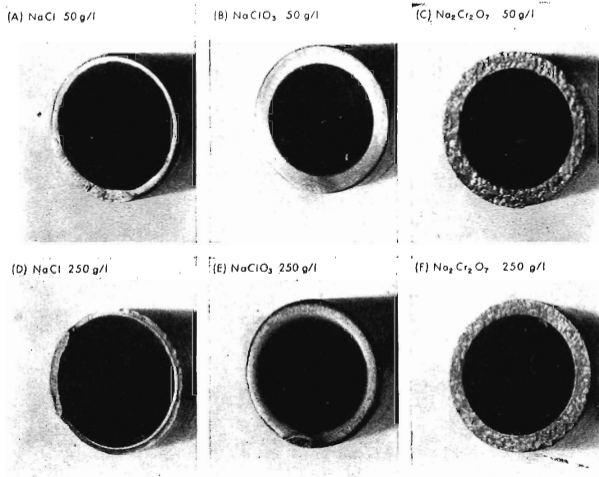


FIG. 5
Photomicrographs of Tube Ends under Same Conditions as in Fig. 4
At an applied potential of 20 V; Na₂Cr₂O₇ tests were run at 30 V.

centration in the NaClO_3 electrolyte. It has been noted in other work⁵ that the ECM metal removal rate in NaClO_3 exceeds that in NaCl at concentrations of NaClO_3 greater than 350 g/l and continues to increase with increasing NaClO_3 concentration up to about 600 g/l.

By studying the photomicrographs of the tube ends to assess the amount of stray cutting and the quality of the surface finish, it is observed that under all conditions the cross-sectional area of all samples machined in NaCl has been reduced from the original value. This behavior gives evidence that cutting on both the inside and outside walls as well as the cross-sectional face of the tube has taken place; if stray cutting were absent, metal removal would take place only on the cross-sectional face. In most cases, the wild cutting had reduced the cross-sectional area to less than half of the original value in NaCl solutions whereas in NaClO_3 solutions very little change in the cross-sectional area had occurred. The difference between these two electrolytes is qualitatively evident from Fig. 4* and 5* without resorting to a quantitative

TABLE III
ECM of 1020-Steel Tube Ends in NaClO_3

Closed circuit voltage V	Length before ECM cm	Length after ECM cm	Metal removal cm	Surface finish	Stray cutting	Remarks
At 50 g/l						
10	5.004	4.991	0.013	excellent	Nil	
15	5.055	4.938	0.117	excellent	Nil	
20	5.029	4.907	0.122	excellent	Nil	
25	5.042	4.514	0.528	—	—	sparking with EDM
30	5.049	—	—	—	—	could not run test
Mechanical component	4.817	4.816	0.001			
At 250 g/l						
10	5.032	4.854	0.178	excellent	Nil	
15	5.070	4.826	0.244	excellent	Nil	
20	5.006	4.760	0.246	good	slight	
25	5.032	4.762	0.270	—	—	a little sparking
30	5.042	—	—	—	—	could not run test
Mechanical component	5.032	5.030	0.002			

* See insert facing p. 688.

term. If such an assessment is desirable, it may be readily calculated from the tube ends and expressed in terms of percent.

Since no ECM takes place in $\text{Na}_2\text{Cr}_2\text{O}_7$ electrolytes, any comparison of tube ends tested in this electrolyte with those in the other electrolytes is of only academic interest.

It is to be noted that ECM operation in NaClO_3 is more advantageous at the higher salt concentrations whereas the best operation in NaCl is in the lower concentrations. This limits NaCl operation to conditions of lower metal removal rates, since any attempt to operate in NaCl at high concentrations results in such an increased stray cutting that geometrical and dimensional control is lost (See Fig. 4A and 5B)*.

Because the data presented in Tables I–III and Fig. 4* and 5* demonstrate that NaClO_3 is a superior electrolyte for ECM operation, it was desirable to find an explanation for this behavior. In an attempt to accomplish this goal, a fundamental approach was taken through the study of polarization curves obtained on soft iron microelectrodes in O_2 -stirred ECM electrolytes to obtain a plausible account of the experimental observations in terms of passivating films.

In general, the data in Fig. 6 show that when a film is present the current is low; when absent, the current is high. Consider first the polarization curve for iron in NaClO_3 (curve 2). At low potentials, iron is dissolved in the active region where the iron surface is relatively free of an oxide film. As the potential is raised to more noble values, the current passes through a maximum value to low current values while the oxide film builds up on the iron surface. In the passive region where the current is very low, the surface is covered by a protective layer of oxide. The composition of this oxide is not clear-cut. Evans⁹ calls it cubic oxide which may be composed

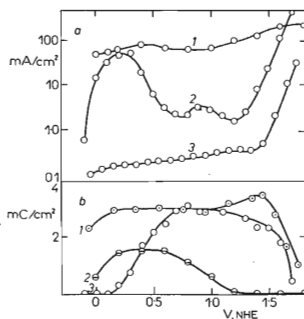


FIG. 6

Steady-State Potentiostatic Polarization Curves for Soft Iron Microelectrodes

a O_2 -saturated solutions of 1 NaCl 2 NaClO_3 and 3 $\text{Na}_2\text{Cr}_2\text{O}_7$ at the higher salt concentrations. NHE. *b* A plot of the thickness of the oxide films formed on soft iron microelectrodes in concentrated solutions of NaCl (2), NaClO_3 (3), and $\text{Na}_2\text{Cr}_2\text{O}_7$ (1) in terms of millicoulombs (mC) of charge per square centimeter determined from constant current stripping pulses as a function of potential.

* See insert facing p. 688.

of either Fe_3O_4 or $\gamma\text{Fe}_2\text{O}_3$ or both or some mixture of oxides^{10,11}. For the sake of simplicity, the film will be referred to as $\gamma\text{Fe}_2\text{O}_3$ in this discussion.

Finally, a potential is reached above which the passive film breaks down and current increases once more in this transpassive region. It is believed that ECM operation takes place in the transpassive region where the passivating film of oxide is virtually absent. Chikamori and Ito¹² have also come to this conclusion. The mechanism for film breakdown may involve the ability of the anion to penetrate and dissolve the oxide film as noted by Hoar¹³.

Under actual ECM operation at the high values of current density between 60 and 200 A/cm², the iR drop across the electrolyte gap between the tool cathode and the workpiece anode may assume very large values. Consequently, the potential drop across the double layer which controls the rate of the anodic corrosion process will be much larger at points directly opposite the cutting face of the tool such as the tube end than at points remote from the tool such as the sides of the tube. At the tube ends, the iR drop is small, and the potential controlling the corrosion process corresponds to potentials in the transpassive region of the polarization curve; at the walls of the tube, the iR drop is so large that the controlling potential falls to values corresponding to those in the passive region of the polarization curve. Therefore, the potential range over which the transition from the passive (no cutting) to the transpassive (cutting) region takes place must be narrow to obtain good dimensional control. This is true for the case of NaClO_3 , and good dimensional control is obtained with this electrolyte (Fig. 4B, 4E, 5B, 5E)*.

With NaCl electrolytes (Fig. 6a, curve 1), large current densities are obtained at all potentials; and although some film formation at the low potentials is indicated in the data of Fig. 6b, the protection provided by this film is very poor. As noted by Hoar¹³, Cl^- ion is a very efficient agent for the dissolution of iron oxide films. Since a protective film is not present on iron in NaCl electrolytes, dissolution can occur at relatively large distances from the cutting face of the tool producing the wild cutting and lack of dimensional control noted in Fig. 5A* and 5D*.

In the case of $\text{Na}_2\text{Cr}_2\text{O}_7$, a very highly protecting film of $\gamma\text{Fe}_2\text{O}_3$ is formed on the iron surface so that very little current flows at the lower potentials. Although a sharp transition exists in the polarization curve (curve 3 of Fig. 6a), this occurs at much higher values of potential than in the case of NaClO_3 (curve 2). As a result, metal removal does not take place at the operating potentials of the other electrolytes (10–20 V). At 30 V (Fig. 5C and 5F)*, where metal is removed, heavy sparking takes place which produces unacceptable surface finished. Here, the metal removal mechanism is by electrical discharge machining (EDM)¹⁴ and/or welding and tearing.

These studies show excellent correlation between the fundamental polarization data and the results of operational ECM experiments. It is concluded that the electro-

* See insert facing p. 688.

lyte which gives good finishes and dimensional control with high metal removal rates must show a sharp transition between the passive and transpassive regions of the polarization curve for a given material. This transition must occur at potentials low enough to avoid surface-damaging sparking. Of the electrolytes studied, NaClO_3 is superior to others in terms of quality of surface finish at high metal removal rates with good dimensional control for the electrochemical machining of many materials, such as low-carbon steels, hardened tool steel, stainless steel, and nickel based high temperature alloys.

REFERENCES

1. Anocut Engineering Co., Elk Grove Village, Ill.; Ex-Cell-O Corp., Detroit, Mich.; Cincinnati Milling Machine Co., Cincinnati, Ohio.
2. Rolls-Royce, United Kingdom; Product Engineering Research Association of Great Britain (PERA), Leicestershire, England.
3. Allison C. R.: Creative Manufacturing Seminar, ASTME (1963-4); Vandenburg G. K., ASTME (1964-5); Rupender R. R. ASTME (1966); Hopfenfeld J., Cole R. R.: ASTME (1966).
4. Bayer J., Cummings M. A., Jollis A. U.: DDC Report AD 450199, Sept. 1964.
5. LaBoda M. A., McMillan M. L.: Electrochem. Technol. 5, 340 (1967).
6. Hoare J. P.: J. Electrochem. Soc. 109, 858 (1962).
7. Hoare J. P.: Electrochim. Acta 9, 599 (1964).
8. Trasatti S.: Electrochim. Metall. 2, 12 (1967).
9. Evans U. R.: *The Corrosion and Oxidation of Metals*, p. 136. St. Martin's Press, New York 1960.
10. Hoare J. P.: *The Electrochemistry of Oxygen*, p. 375. Interscience, New York 1968.
11. Nagayama M., Cohen M.: J. Electrochem. Soc. 109, 781 (1962); 110, 670 (1963).
12. Chikamori K., Ito S.: *Denki Kagaku Oyobi Kogyo Butsuri Kagaku* 37, 602 (1969).
13. Hoar T. P.: Corrosion Sci. 7, 341 (1967).
14. Anonymus: Machinery 62, 139, No 9 (1956); 169, No 10 (1956).