

# THE BELL SYSTEM TECHNICAL JOURNAL

---

VOLUME XXXIV

NOVEMBER 1955

NUMBER 6

---

*Copyright, 1955, American Telephone and Telegraph Company*

## Silver Migration in Electrical Insulation

By G. T. KOHMAN, H. W. HERMANCE, and G. H. DOWNES

(Manuscript received May 17, 1955)

*Silver migration may be defined as a process by which silver, when in contact with insulating materials under electrical potential, is removed ionically from its initial location, and is redeposited as metal at some other location. This process requires adsorption of water on the insulation surface. Silver is unique in this respect in that it is easily oxidized and reduced and does not passivate. Other metals do not present a practical migration hazard. Presented herein are examples of actual experience wherein silver migration caused trouble, and an explanation of this phenomenon based upon chemical and physical considerations and related laboratory evidence. It is concluded that silver should be used with great caution under the conditions noted.*

### INTRODUCTION

Silver or silver plated metals, because of the favorable electrical and chemical properties of silver, have application in communications systems and throughout the electrical industry. When fabricating apparatus component assemblies, it is frequently expedient to assemble the silver parts in a manner such that they are in intimate contact with insulating materials such as phenol fiber. When standing electrical unipolar potential and atmospheric moisture are present, the silver may migrate. Silver migration may be defined as a process by which silver, when in contact with insulating materials under electrical potential, is removed ionically from its initial location, and is redeposited as metal at some other location. The redeposition occurs in two principal ways, namely;

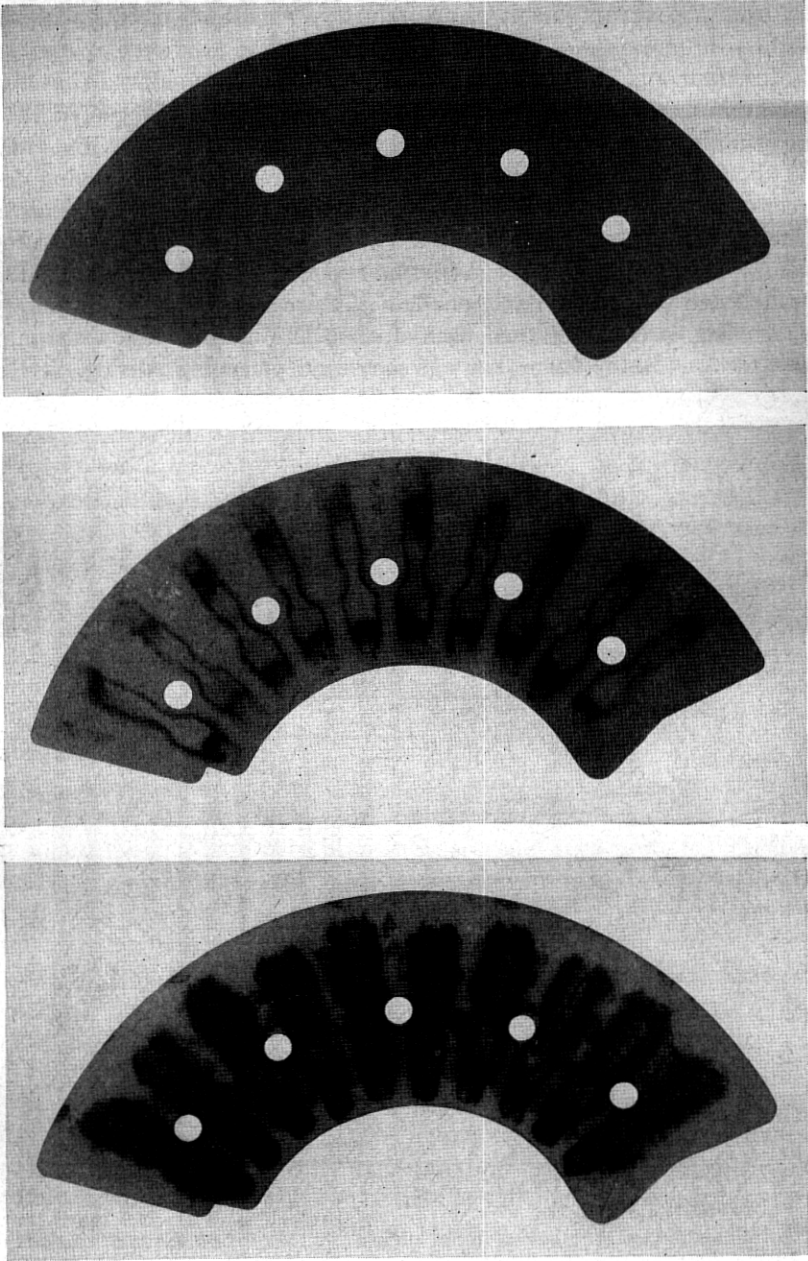


FIG. 2 — Step-by-step bank phenol fiber separators illustrating silver migration.

An equipment unit consists of either 10 or 11 banks and the associated connecting wiring, and this unit is termed a bank multiple. The initial insulation resistance of a bank multiple when new is in the order of 1,000 megohms, and the resistance can degrade to a value of approximately 0.03 megohms in the entire talking path through an office before pulsing failures are likely to occur. By testing banks in the laboratory it was found possible in thirty days, by employing accelerated test conditions of 130 volts at 90 per cent relative humidity, to duplicate the amount of silver transferred into the insulator in four years of service.

There is also a possibility of through migration into the insulator to which the terminals are attached, as indicated by Note 3 of Fig. 1. This possibility can be prevented or stopped by grounding the metal separator, thus eliminating the potential difference between the tip terminal and the metal separator.

### *Lateral Migration*

In the step-by-step bank system there is another migration path, illustrated by Note 4 on Fig. 1, which is termed "lateral migration". This occurs in only a relatively few cases and is most prevalent where the standing potential on laterally adjacent terminals in the idle condition is of opposite polarity. This situation occurs on connector switch banks in the case of certain party lines. This particular manifestation of migration generally takes the form of a deposit of silver, of superficial depth, on the front edge of the insulator to which the terminals are attached. In aggravated instances there may be some penetration back into the insulator. Deposition of silver along the front edge of the insulator can bridge terminals laterally and has caused crosstalk or a trouble condition which involves premature tripping of the ringing on a subscriber line, in which case a "no ring" situation results. Fig. 3 shows an insulator of this type which has failed dielectrically.

The lateral migration condition just described is the usual one with respect to the insulator to which the terminals are attached. However, there is another migration condition which has resulted from a slightly different bank construction. In some of the earlier banks which had silver plated terminals, the terminals were attached to a strip of varnished cambric which rested against a phenol fiber insulator. In this case the silver migrated into the cambric in a manner as shown in Fig. 3.

### *Silver Charged Dust*

There is one further manifestation of silver migration which has occurred very infrequently in the step-by-step system. This involves a

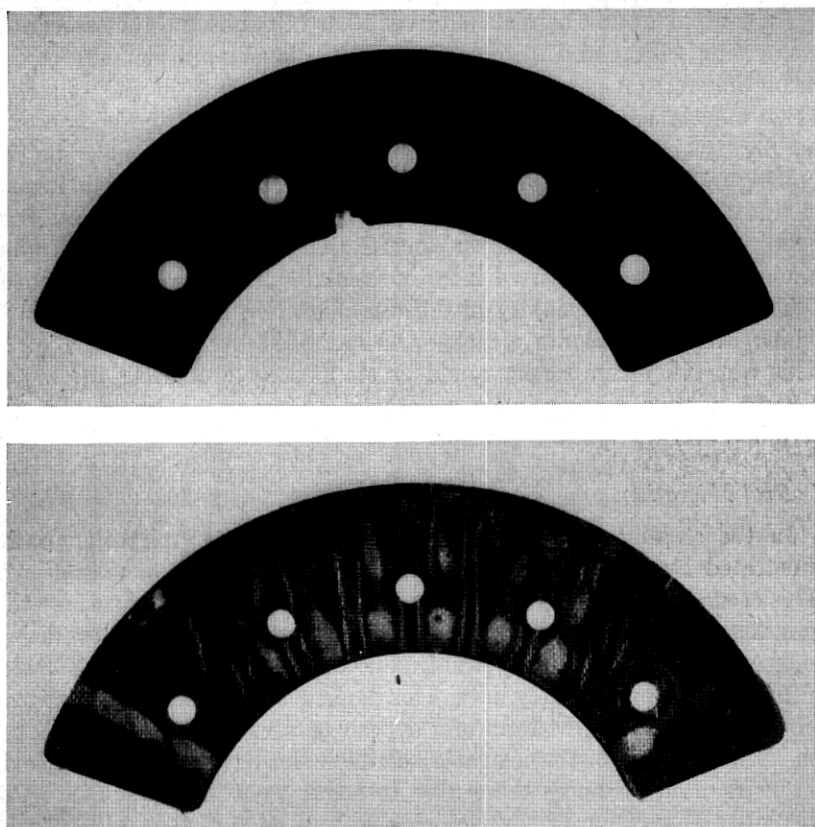


FIG. 3 — Step-by-step system — illustrating migration in insulators to which the terminals are secured.

condition in which substantial quantities of dust have been allowed to accumulate in the bank interspaces between terminals laterally. In this case the dust may become loaded with silver and this can result in sufficient resistance coupling between terminals to produce some crosstalk. Presence of silver in these dusts was verified by chemical analysis.

#### *Panel Dial System*

Another application of silver plated bank contacts was in the panel dial system. At one period of manufacture the contacts in the banks, through which talking connections are established, were silver plated in their entirety. Later, the contacts were plated in a manner such that the silver was omitted from the terminal area in contact with the insu-



lation. Still later, following the introduction of silver multiple brushes, it was no longer necessary to plate the associated bank terminals and silver plating of the brass terminals was discontinued. In certain of the frame circuits, standing 48 volt dc potential is present during the idle circuit condition in a manner similar to that of the step-by-step system. The bank construction differs materially from that of the step-by-step system. The panel bank consists of long continuous metallic strips of terminals which are insulated from each other by a wood pulp paper impregnated with asphalt. More recently, some difficulty from silver migration has been experienced in this system as manifested by lowered insulation resistance or momentary short circuits. Silver migration in this instance usually takes the form of very fine silver filaments which grow on the surface of the paper insulation. Bank vibration and dimensional changes in the bank structure, resulting from shifts in the level of relative humidity, may cause the fine silver filaments to break or become reoriented thus producing an unstable electrical leakage condition. This problem is in the investigative stage.

### *Field Measurements*

Measurements by field maintenance personnel in step-by-step offices have generally been made with a 1,000-ohm per volt 100-volt scale voltmeter using 100 volts of test battery. Measurements are thus in terms of volts of leakage which is converted to ohmic resistance. Many readings have been taken which show varying degrees of leakage. In conducting more detailed studies of a field nature, a megohm bridge is used to obtain more accurate resistance data. This instrument measures ohmic resistance directly. Table I lists typical measurements in a step-by-step office, when using a megohm bridge, on banks where migration had not reached an advanced stage.

The readings in Table I show the insulation resistance for a bank multiple and represent lateral migration leakage wherein the minimum distance between edges of the terminals is 0.120". The silver plated multiples had been in service for 9 years. At the time the measurements

TABLE I — TYPICAL MEASUREMENTS IN A STEP-BY-STEP OFFICE

Measurement Points	Insulation Resistance in Megohms	
	Silver Banks	Brass Banks
Tip to Tip and Tip to Ground.....	309	1177
Ring to Ring and Ring to Ground.....	416	983

were taken the temperature was 87°F and the relative humidity 59 per cent.

These data serve to illustrate the gradual deterioration of the insulation resistance of silver plated contact bank multiples. Measurements made in the laboratory on individual contacts show that the insulation resistance tends to remain at a relatively high level until the point of dielectric failure is imminent. This leads to the conclusion that when evaluating the silver migration hazard with respect to insulating materials, the test should be made in terms of both dielectric strength and insulation resistance.

### *Field Aspects of Laboratory Testing*

The principal objectives of the material laboratory testing program were as follows:

1. To verify the fact that silver migration was present.
2. To study the factors which affected the rate of migration.
3. To determine whether temporary remedial measures could be devised.
4. To study materials to determine those which would not be subject to silver migration and which could be used to replace defective insulators in service.

This program was carried to a successful conclusion.

Verification of the fact that silver migration had occurred was simple and conclusive.

The factors which affected the rate of migration were found to be the nature of the insulating material, the magnitude of the standing unipolar dc potential, the elapsed time of standing voltage and the level of relative humidity. Phenol fiber and phenol fabric were found to be particularly susceptible to silver migration. Increasing the voltage and maintaining a high level of relative humidity were found to accelerate migration. Many insulating materials contain salts which, depending upon their nature, may or may not affect the rate of migration. It was found that the relative humidity must be maintained at a very low value to completely inhibit migration. The development of migration in the field was most severe in high humidity areas. Leakage readings made during periods of high humidity were always greater than similar measurements made at low humidities. Such expedients as reversing the dc potential were tried but it was found that a constantly reversing potential at a rapid rate of once per second was necessary before substantial benefit could be realized.

It is fortunate that the progress of migration is rather slow at 48 volts,

and time was available to devise remedial measures. A number of such measures were investigated most of which proved ineffective, and with one exception, none was found which had practical application. The one method which appeared promising was to subject the phenol fiber to heat. While this treatment did not effect a permanent improvement, it did restore insulation characteristics for an appreciable period of time.

Many materials were studied to determine their silver migration susceptibility. A surprising number of these materials reacted unfavorably. Two materials of practical value were found; namely, a special rubber composition sheet material, with the surface sandblasted, and an aceto-butyrates plastic sheet material. Neither of these materials was found to be subject to either through or lateral surface silver migration.

#### FIELD REMEDIAL MEASURES

##### *Heat Treatment of Banks*

The first installation in which silver migration was experienced required that remedial measures of some sort be made available promptly if replacement of certain equipments was to be avoided. The only method which could be recommended on short notice, based upon laboratory tests, was to subject the banks to heat. It was predicted that sufficient improvement in the insulation characteristics would result to correct service troubles. Furthermore it was hoped that the improvement would be effective for a sufficient period of time to permit the determination of a more permanent remedy. The heat treatment method was used and in most instances improved the insulation characteristics to a point where service difficulties were no longer experienced and the improvement persisted for a time sufficient to develop a more permanent remedy. Hot air at a temperature of approximately 350°F was forced through each bank for a period of about one-half hour. Fig. 4 shows the heat treatment facilities in place on a bank multiple.

##### *Replacement of Bank Separators*

Silver migration in the step-by-step system has affected principally the phenol fiber separator between the T and R terminals. The problem was to discover an insulating material which would not be subject to through migration. The separator may be replaced quite readily by dismantling the bank, removing the degraded insulators and inserting new insulators. This is a simple procedure as contrasted with replacement of the entire bank multiple.

The material selected initially for the replacement insulator was a

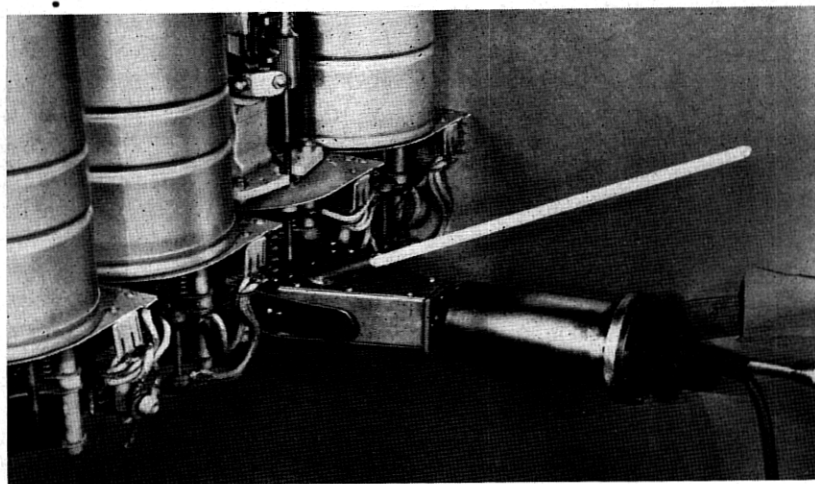


FIG. 4 — Equipment for heat-treating step-by-step banks.

special hard rubber composition with the flat surfaces sandblasted. Insulators of this type have been used successfully and after several years of service have exhibited no silver migration contamination.

For a short period of time insulators of the same rubber composition, with the sandblasting omitted, were tried, but crosstalk troubles developed in service in a relatively short time. While this rubber was not subject to through migration it did develop a lateral migration condition on the surface as illustrated by Fig. 5. It was found that the surface contamination consisted of silver and silver sulphide. It was again necessary to replace these insulators.

By this time a material superior to rubber had been tested and qualified as being free from either lateral or through migration hazards. This material was an aceto-butyrate composition sheet. It has been employed for all subsequent replacements and has proven to be free from silver migration impairment after several years of service.

### *Lateral Migration*

This condition usually manifests itself in the step-by-step system as a continuous deposition of silver of superficial depth on the front edge of the insulators to which the terminals are secured. Correction of this condition involved the development of tools and procedures for physically removing this thin layer of silver. Scraping tools were recommended and used with considerable success for correcting this condition. For those

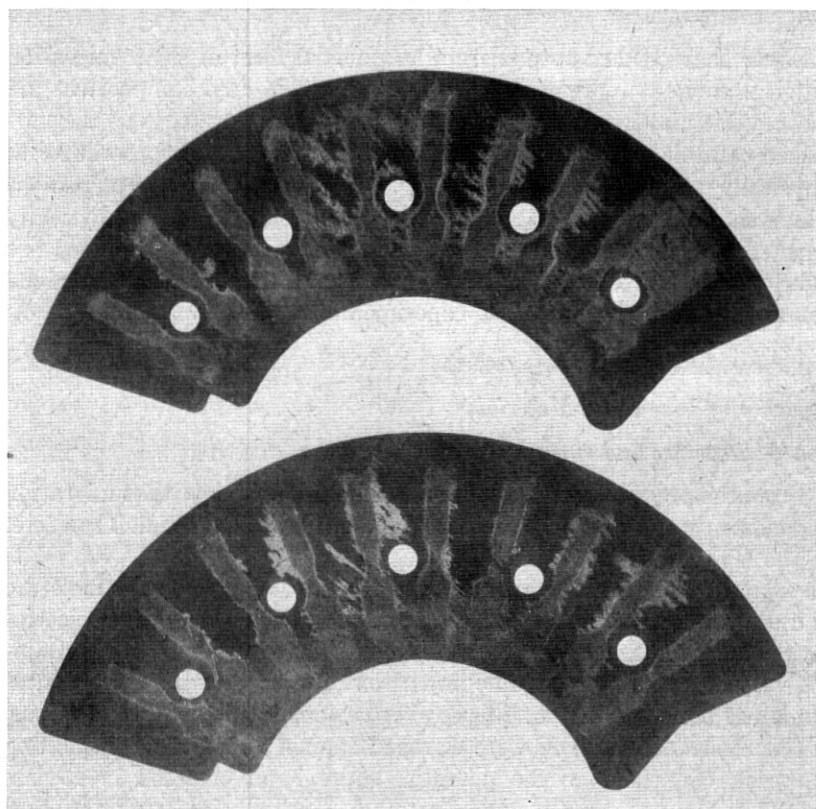


FIG. 5 — Step-by-step bank hard rubber separators illustrating lateral surface migration.

few cases where the silver had penetrated into the insulator to an appreciable distance back from the front edge, the scraping technique was ineffective. For the occasional replacement of such insulators, a set of tools and fixtures was made available to make it possible to remove and replace an individual insulator. In this operation, which is more complex than the replacement of a removable bank separator for through migration, the bank was dismantled, the terminals were broken loose from the phenol fiber insulator and an aceto-butyrates insulator was used for replacement. This procedure would be too costly if many insulators in a bank multiple were affected. Thus in extreme cases of lateral migration affecting a multiplicity of insulators in a bank multiple, replacement of the multiple was the only practical expedient.

### *Silver Charged Dust*

Silver charged dust results from an unusual form of silver migration but it is difficult to combat when it occurs. The dust compactions are inaccessible and they adhere firmly to such insulating parts as the varnished cambric component of certain banks, and cleaning procedures to physically remove the dust cannot be employed. The only expedient which shows promise is to apply a high voltage discharge to physically burn silver compounds out of the compacted dust. Very little need has developed for a remedy for this condition and the burn-out technique has not progressed beyond the experimental laboratory stage.

#### CHEMICAL AND PHYSICAL ASPECTS

### *Behavior of Insulating Materials*

#### *a — Structure and surface*

From the preceding discussions and evidence, it is clear that migration depends on water and on structure of the insulating material. Therefore, in the laboratory investigations of the process, observations were made on a group of materials which differ widely in their affinity for moisture and also in their structure. To establish the possible relation of electrolytic contamination, observations were also made on materials containing varying amounts of soluble impurities. The experimental procedures made use of controlled humidities over various saturated salt solutions.

Bar electrodes of silver were clamped against strips of the insulating material, connected to the potential supply and enclosed in a glass chamber. Fig. 6 shows the clamp assembly. For lateral migration studies, spacings of  $\frac{1}{8}$ " to  $\frac{1}{2}$ " were used.

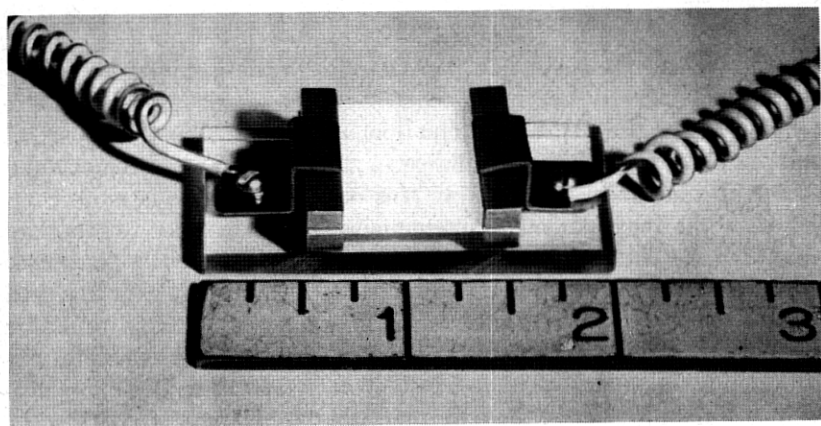


FIG. 6 — Electrode clamping assembly for migration studies.

TABLE II — MIGRATION TEST WITH SILVER ELECTRODES ON VARIOUS MATERIALS AT 91 PER CENT R.H.

Material	Thick- ness	Applied Voltage	Resistance, Megohms, Final	Length of Test in Hours	Behavior
	<i>inches</i>				
Polystyrene (G.E. No. 1421)	5/32	200	$10^5$	3,100	No migration
Tenite I	0.010	200	$10^5$	5,300	Very slight migration
Tenite II	0.018	200	$10^5$	5,300	No migration
Hard rubber separator sandblasted*	0.019	200	$10^6$	3,100	No migration
1-Stage unfilled Bakelite resin (No. BR-15,055)	0.075	200	$10^6$	1,900	No migration
2-Stage unfilled Bakelite resin (No. BR-1,922)	0.065	200	$3 \times 10^4$	1,900	Very slight migration
Ruby mica	0.002	200	2	3,700	Slow surface migration
1 S phenol fiber	0.019	200	0.01	2,600	Appreciable migration—started after 140 hours
Microscope slide glass	1/32	200	$10^5$	4,000	Slight surface migration
Absorbent kraft paper	0.006	45	0.01	70	Appreciable migration
White cotton rag paper	0.007	45	0.01	70	Appreciable migration
White a-cellulose wood-pulp paper	0.007	45	0.01	80	Appreciable migration
Whatman filter paper No. 1	0.007	45	0.01	90	Appreciable migration
Lens paper	0.001	45	0.01	48	Appreciable migration
Cellophane	0.001	45	0.15	7	Appreciable migration

\* 67.5 per cent Smoked Sheet, 30 per cent Sulfur.

A dc potential of 45 volts was used in most cases. The temperature was maintained at 35°C and frequent measurements of resistance were made. In some instances, where the resistance remained high, the voltage was later increased to 200.

Table II shows the comparison of migration in a variety of materials at 91 per cent R.H. The change in resistance for these materials is shown graphically in Figs. 7 and 8. The order of the materials in Table II is approximately that of their affinity for moisture. As expected, this corresponds very closely to the extent of silver migration. The extreme range of behavior is indicated by comparison of polystyrene, which shows no migration at 200 volts after 3100 hours, retaining a final resistance of  $10^5$  megohms, with cellophane the resistance of which falls to 0.15 megohms in 7 hours at 45 volts. Tenite I and II show little or no migration under the most severe conditions. Sandblasted hard rubber



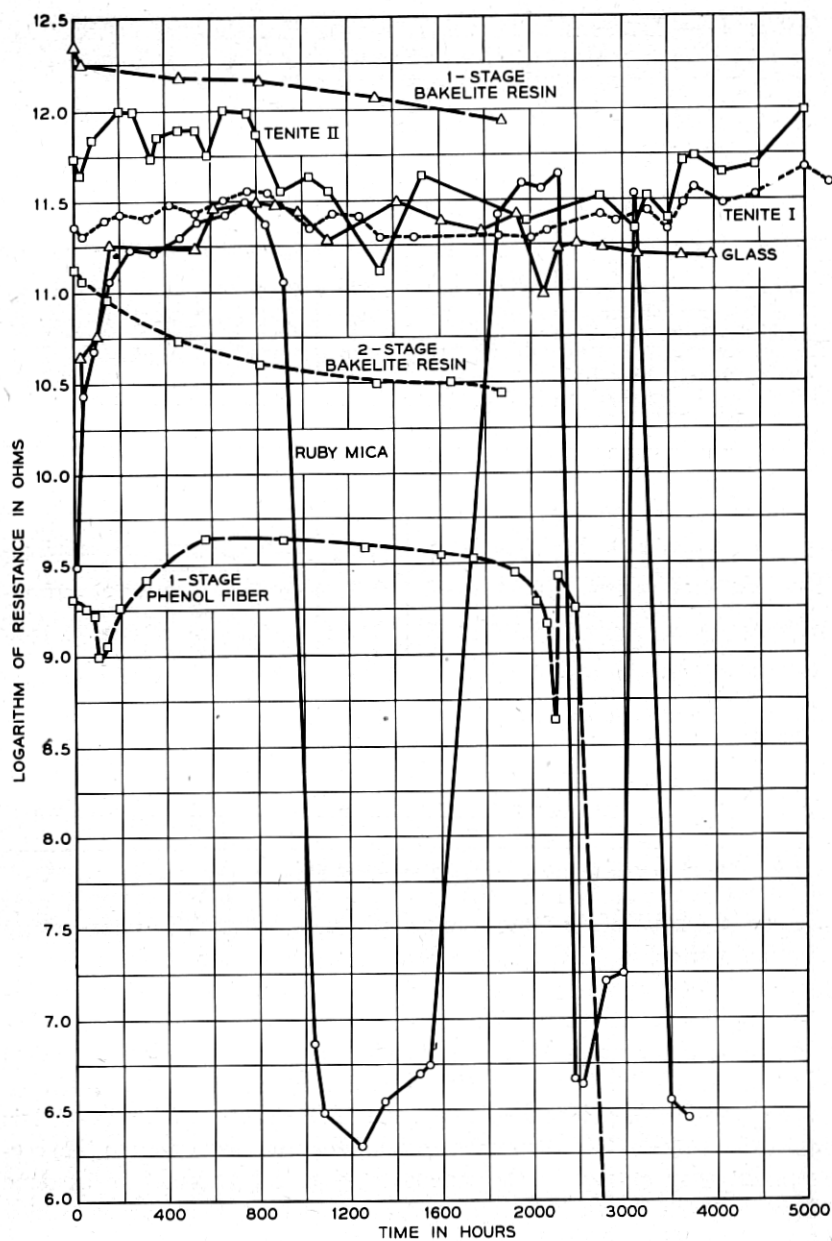


FIG. 7 — Silver migration in various insulating materials.

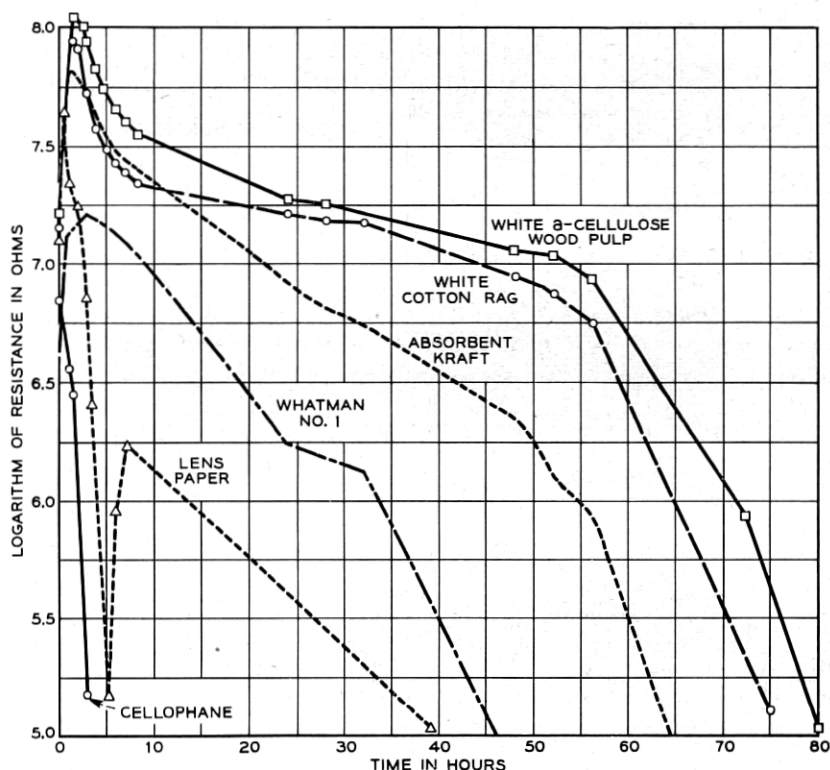


FIG. 8 — Silver migration in cellulosic materials.

which has a somewhat greater affinity for moisture than polystyrene also shows no migration. Slight migration was observed in two-stage unfilled Bakelite resin as compared with none in the single-stage resin. This is probably caused by a slight excess of catalyst usually found in the two-stage material, the decomposition products of which tend to dissolve silver in the presence of moisture. Mica and glass, the surfaces of which are much more hygroscopic, exhibit surface migration visually as well as electrically.

The cellulosic materials which are considerably more hygroscopic than any of the other materials tested also exhibit extreme silver migration. In these cases, because of the porosity of the material, both lateral and through migration are observed. Furthermore, the high purity papers, such as the absorbent Kraft paper and the white cotton rag insulating papers show less migration than the less pure lens paper and cellophane.

The appearance of the specimens after test is shown in Figs. 9 and 10.

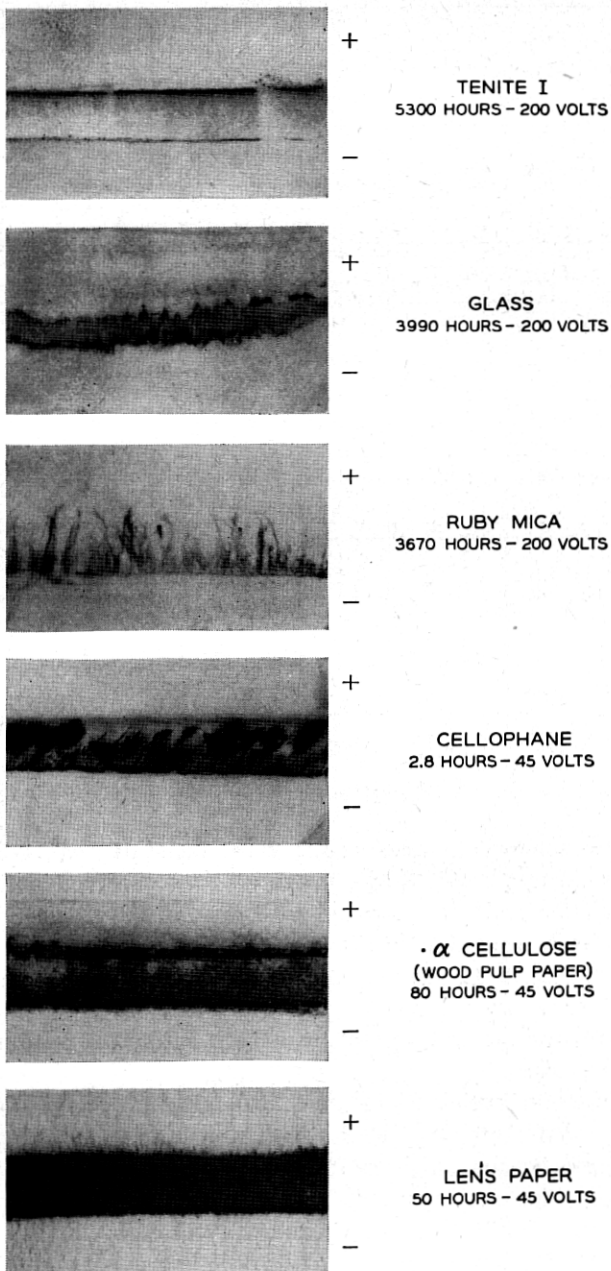


FIG. 9 — Silver migration patterns in various materials at 91 per cent R.H.

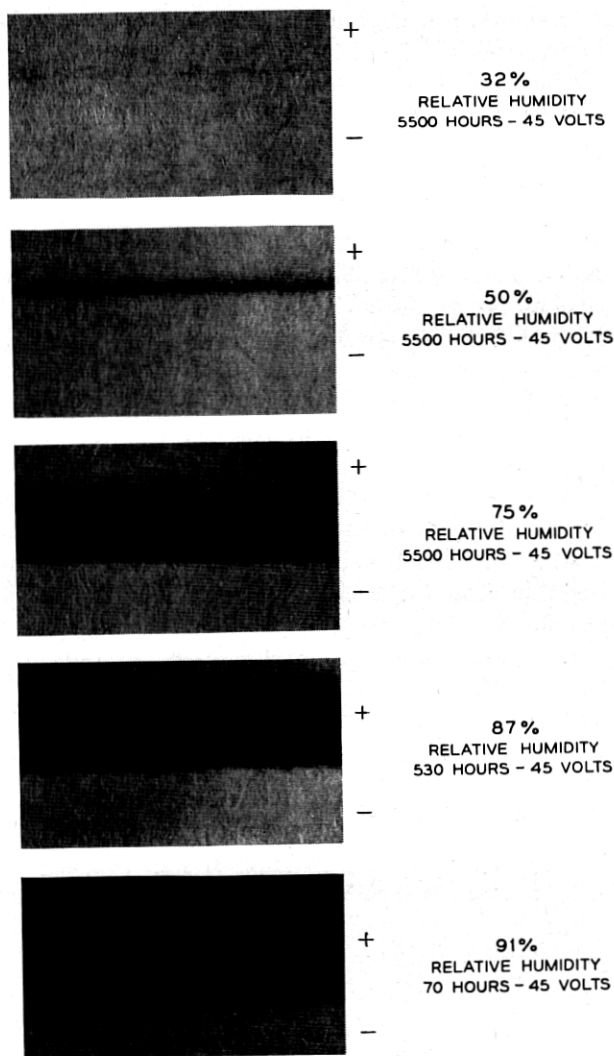


FIG. 10—Silver migration in kraft paper at 45 volts and various relative humidities.

Microscopic examination reveals a dendritic growth from the cathode (—) and a brown deposit at the anode (+). As shown by Figs. 9 and 10 and the data of Figs. 7 and 8, the deposits grow until they bridge the electrodes causing a sudden drop in resistance which in some cases is followed by a sudden increase indicating partial destruction of the conducting

paths. The mechanism of destruction may involve recrystallization of the silver brought about by resistance heating. It is well known that at moderate temperatures thin conducting silver films recrystallize to form discontinuous deposits. Since the silver is not eliminated by this process the paths are usually quickly reestablished, resulting in another sudden drop in resistance. These experiments were not continued to the point of dielectric failure.

In the case of cellophane, manufacture involves extrusion through a slit. Orientation of the linear cellulose molecules occurs in the direction of this extrusion. As seen from Fig. 9, migration does not follow the shortest path but the direction is determined by the orientation of the molecules which in this case is at 45 degrees from the applied field. This illustrates the tendency of the ions to follow the path of highest moisture concentration which is determined by the distribution of hydroxyl groups in the cellulose molecules.

In the 1S phenol fiber lateral migration is readily apparent after 1,000 hours. The dendritic growth extending from the cathode follows the cellulosic fibers until it reaches the anode. Fig. 11 shows the appearance at the end of this time. Little change in resistance was observed until the electrodes were bridged, when the resistance dropped abruptly. This appears to be characteristic of lateral migration in impregnated fibrous materials, and for this reason resistance measurements are not a reliable indication of the progress of migration.

Comparison of the unimpregnated fibrous base (paper, for example) with the same materials into which resins have been introduced (phenol fiber) shows the marked effect of the latter in reducing the rate of mi-

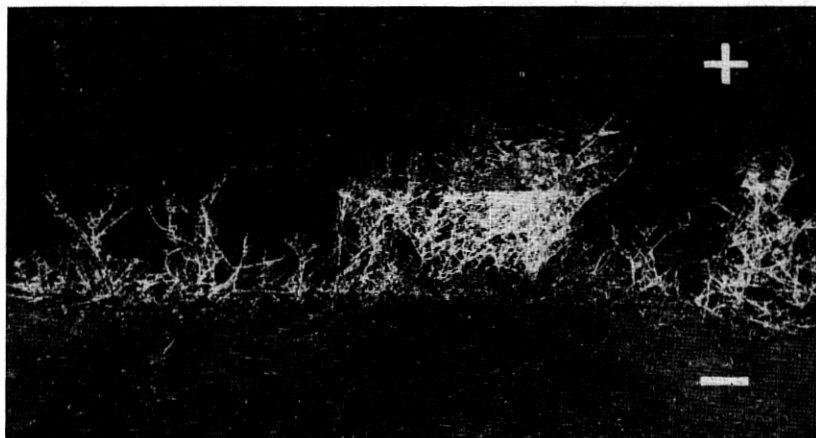


FIG. 11 — Lateral migration on 1S phenol fiber after 1,000 hours, 91 per cent R.H. photographed by reflected light to show silver dendrites.

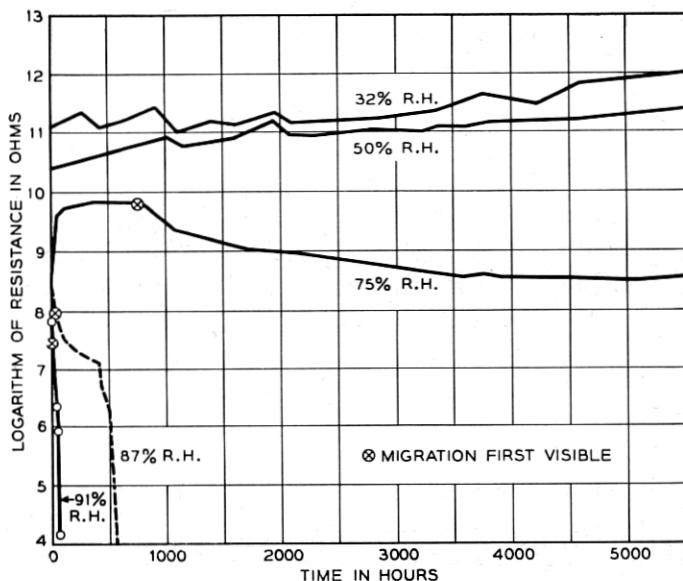


FIG. 12 — Resistance of kraft paper as related to humidity.

gration. Such impregnants restrict ion mobility, probably in two ways: (1) They reduce the rate of moisture penetration, thus providing protection against transient high humidities. (2) They interpose barriers between the individual fibers. From the practical standpoint, however, such improvement is still not effective enough as evidenced by the occurrence of silver migration in phenol fiber in the field.

#### *b — Moisture*

As has been mentioned, the affinity of surfaces for water varies widely. The surfaces of non-polar materials such as polystyrene and polyethylene have only a slight attraction for water which is reflected in a high angle of contact between liquid water and the solid surface and also by a low heat of adsorption. On the other hand, the polar hydroxyl group in cellulosic materials gives them a very high affinity for moisture. The dependence of silver migration in Kraft paper on relative humidity is shown in Fig. 12. The insulating materials promote silver migration primarily by providing surfaces on which it is possible for moisture to liquefy at relative humidities below 100 per cent. It is very probable that for silver ions to form and move on a surface, at least a monolayer and possibly two must be present.\* To cause this amount of water to con-

\* For a discussion of mobility in adsorbed layer see Statistical Thermodynamics, Fowler and Guggenheim, Cambridge University Press, 1939, page 421.

dense on surfaces differing as widely as cellulose and polystyrene requires widely different relative humidities. Contamination with water soluble compounds is also an important consideration. Since contaminants and degradation products are inevitably present on cellulose surfaces, such contamination may increase the quantity of water which will condense at a given relative humidity. The influence of relative humidity on migration would be expected to decrease rapidly below approximately 30 per cent, since less water is normally adsorbed and since the solubility of most compounds is such that they do not cause condensation of water below this humidity.

### *Microscopic Studies*

Microscopically the pattern of silver deposit, when migration occurs, will vary depending on the structure of the insulating material, its chemical composition and whether or not the electrical field acts *across the surface or through* the insulator. The intensity of the field and the available moisture will influence the rate, the manner and the extent of deposition.

When the insulator has an impregnated fibrous structure such as phenol fiber, phenol fabric or asphalt impregnated paper, migration progresses along the cellulose-impregnant interface. In typical manifestations, fine filaments as small as 2 to 5 microns in diameter grow out from the cathode along the individual fiber surfaces toward the silver anode. Eventually these filaments reach the anodic area and complete tenuous metallic paths. Resistance measurements have been made on areas where a multiplicity of such paths exists. In the final stages, when potential is present, the resistance is very erratic, falling, then rising sharply in a matter of seconds. This behavior suggests a continual making and breaking of the filamentous contacts on a micro-scale.

The paths from cathode to anode may be relatively direct in the case of materials in which the fibers are arranged in an orderly structure. Such materials are the impregnated fabrics (phenol fabric, varnished cambric, etc.). In these the impregnant rarely if ever reaches completely into the twisted fibrous bundles forming the threads, and almost straight line paths thus are provided. Materials having the fibers in random orientation such as paper or felt, on the other hand, may provide much longer, more tortuous paths from cathode to anode. In such felted materials, a path is formed only by chance overlapping or crossing fibers with no resin barrier between them. Eventually a circuitous chain is completed from cathode to anode.

Where migration occurs *through* an impregnated paper, the paths are



even more tortuous. Phenol fiber, for example, is made up of several layers of Kraft paper, impregnated with phenolic resin and cured under pressure. The fibers are oriented roughly in the plane of the paper lamination and a path for migration normal to the plane is afforded only when a chain of fibers meets in unimpaired contact at each of the lamination interfaces.

When thin specimens of phenol fiber exhibiting migration are examined microscopically by transmitted light, the structure of the silver deposits can be seen fairly clearly. In the anodic area the fibers have a uniformly blackened, non-lustrous appearance suggestive of deposition of silver by chemical or photochemical reduction. This is not unreasonable since reducing agents such as aldehydes are very likely present in small quantities in the resin and the paper itself may have reducing properties. In advanced stages, the blackness seems to diffuse out from the fibers to invade the resinous material. These colloidal deposits may end close to the anode or they may extend practically to the cathode, depending on the particular specimen of phenol fiber, the conditions of transmitted light, voltage and duration of the migration.

The fibers in contact with the cathode, on the other hand, show silver having a quite different structure. Here the deposits have a decided metallic lustre and follow the fiber-resin interface without diffusion into the latter. Under 200 to 400 magnifications, it can be seen that the silver consists of a fine network of metal growing out from the cathode mostly on the face of the fiber but occasionally found growing in its central canal. Where fibers cross, the silver dendrites often change their course and follow a new fiber, the process being repeated many times as the metal grows out into the available ion paths. The net result is a tree-like macro structure made up of dendritic micro structures on the individual fibers. In Fig. 13 are shown individual fibers with the fine dendrites of silver growing on them. These fibers were obtained from a panel system bank insulator in service. The asphalt impregnant was removed by extraction and the paper teased apart in a suspending fluid. Fig. 14 shows a single cotton fiber which was stretched between silver anode and cathode wires in 98 per cent humidity at 45 volts. After 36 hours a cathodic outgrowth of silver was formed in the canal of the fiber. The anodic end of this fiber showed only a structureless transparent brownish stain.

### *Electrochemical Mechanism*

The experiments and observations to this point confirm the reproducibility of migration in or on a wide variety of materials, the only requirements being a standing potential and high humidity. In order to obtain



FIG. 13 — Paper fibers removed from cathodic area showing dendritic silver deposits.

a better understanding of the nature of silver migration, a series of experiments was carried out with filter paper which was relatively free of impurities. In this way, electrolytes, reducing agents and other complicating substances present in commercial materials are largely eliminated. The absence of impregnating resins also facilitates observation of the process both microscopically and microchemically.

CS&S No. 598 paper was clamped between silver bar electrodes at

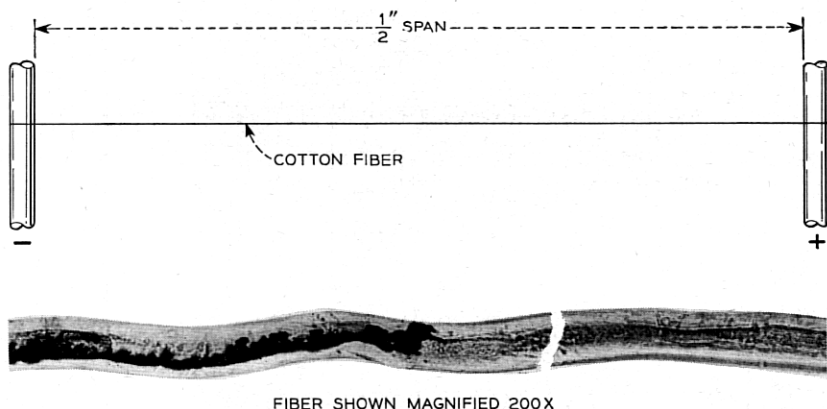


Fig. 14 — Single cotton fiber stretched between anodic and cathodic silver wires showing cathodic silver deposits in central canal, 45 volts, 98 per cent R.H., 36 hours.

98 per cent relative humidity. The spacing between the electrodes was  $\frac{1}{2}$ ", across which a 45 volt potential was maintained. Fig. 15 shows the condition after 6 hours. Dendrites of silver have grown out from the cathode about halfway to the anode. Outward from the anode is a stained area having a relatively sharp boundary. When first observed, this area is yellowish brown in color but in daylight it changes to a purplish gray, suggesting photo-reduction of a silver compound.

A simple explanation which takes into account these basic observations is the following:

In the electrical field provided, silver ions tend to leave the anode in the water film adsorbed on the cellulose fibers. Hydrogen ions collect around the cathode, where initially their discharge maintains electrical balance. Hydroxyl ions move toward the anode but encounter the silver ions moving from it. A region occurs close to the anode in which the product of the concentrations of silver and hydroxyl ions reaches the solubility product for silver hydroxide and a colloidal precipitate is formed. The unstable silver hydroxide probably decomposes immediately to silver oxide,  $\text{Ag}_2\text{O}$ , producing the dark, structureless deposit already described, around the anode. Subsequently the silver oxide may be reduced by light or by reducing agents present in commercial insulating materials or even slowly by the cellulose itself.

Thus the concentration of the silver ions leaving the zone of  $\text{Ag}_2\text{O}$  precipitation will be regulated by the equilibrium:



The solubility product of silver hydroxide ( $\text{Ag}^+ \times \text{OH}^- = K_{\text{AgOH}}$ )

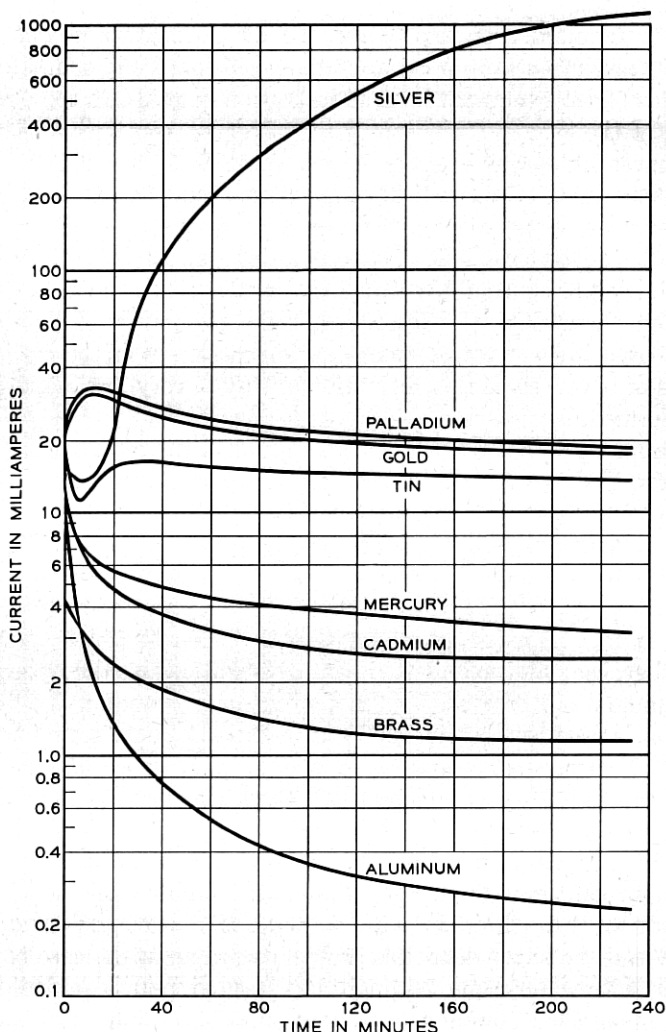


FIG. 16 — Current-time curves for various metal electrodes using moist filter paper, 45 volts.

between. The sandwich was placed under 40,000 pounds pressure to establish good reproducible contact and a 45 volt potential was maintained. In this way sufficient current flow was obtained for direct measurement directly with a milliammeter.

The initial current flow was between 10 and 30 milliamperes for all the metals. For gold and palladium, this level held fairly constant

throughout the experiment. For the base metals (brass, Cd, Al, Hg, Sn) the current dropped off rapidly to lower levels. Silver alone was characterized by a continual rise in the current to a level well above one ampere, at which point considerable heating was apparent.

In each case, the paper sheet next to the anode was removed and tested for the anode metal. The base metals all gave indication of electrolytic transfer, but this was confined to the topmost paper layers in direct contact with the anode and amounted to only a few micrograms. The gold and palladium showed no detectable transfer.

In the case of the silver, the whole pad was filled with reduced metal, from the cathode sheet to the anode.

Thus, it would appear that electrolytic solution of the base metals does occur in the presence of moisture only, but the process is quickly arrested by the formation of highly insoluble, passivating films which seal off the metal effectively. When the paper is removed, part of this film is separated with it and can be detected with sensitive reagents. Gold and palladium having higher oxidation potentials do not dissolve and no passivating films are formed, but rather, oxygen is liberated at the anode, the process producing a fairly constant, low level of current flow.

Silver, on the other hand, dissolves anodically in the presence of moisture alone but is incapable of forming an effective passivating film under such conditions. The oxide formed at the anode is relatively soluble and does not impair greatly the movement of silver ions.

The unique migration behavior of silver, just as its unique value in photography, is probably related to the low free energy of oxidation and reduction reactions. The free energy of formation of the oxide is only  $-2,395$  calories compared with  $-26,000$  for copper oxide. Thus silver is readily dissolved anodically but the resulting ions are easily reduced to the metal, both cathodically and by chemical agents.

### *Inhibiting Techniques*

In addition to the remedial approaches already discussed for equipments in service, there remains the question of improving the properties of insulating materials to resist silver migration in new equipment design. In materials having a fibrous base, three approaches are suggested:

(1) Improvement of resin impregnation to isolate fibers more effectively, thus preventing through paths. From the study of the paths observed in actual migration, it seems quite evident that a more thorough impregnation of the paper, especially at the surfaces and at the inter-

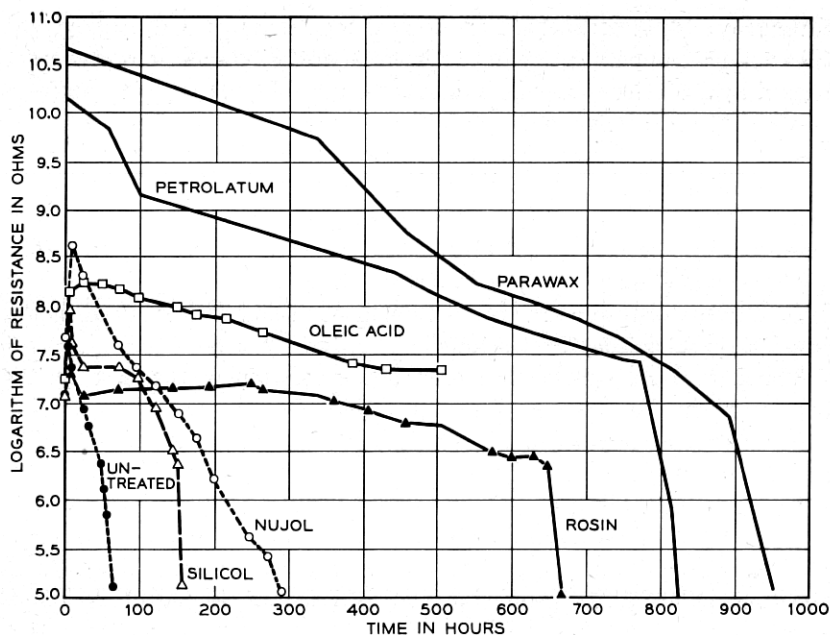


FIG. 17 — Effectiveness of various impregnation treatments in preventing silver migration.

faces between the individual sheets of laminated materials, would greatly reduce the fibrous paths available for migration. Interleaving with a thin sheet of a suitable impervious plastic might provide an effective barrier despite the existence of the fibrous paths on either side.

(2) Treatment to prevent adsorption of water. Pretreatment of fibrous surfaces with water-repellant agents might be expected to reduce silver migration. On the whole, while some reduction was obtained, the results were disappointing. Fatty, waxy and resinous materials as well as silicones and chlorosilanes were tried with varying degrees of retardation but none was sufficiently effective to be practical. Fig. 17 summarizes the performance of a number of these treatments.

(3) Incorporation of silver precipitating agents in the insulation. If a reagent could be introduced into the insulator which would capture the silver ions by precipitation, reduction or sequestration, migration might be retarded to a practical degree. Such a reagent itself would have to be practically non-conducting and its effectiveness would depend on how much of it could be introduced in the migration path. Reducing agents such as aldehydes, hydroquinone, pyrogallol, and hydrazine,

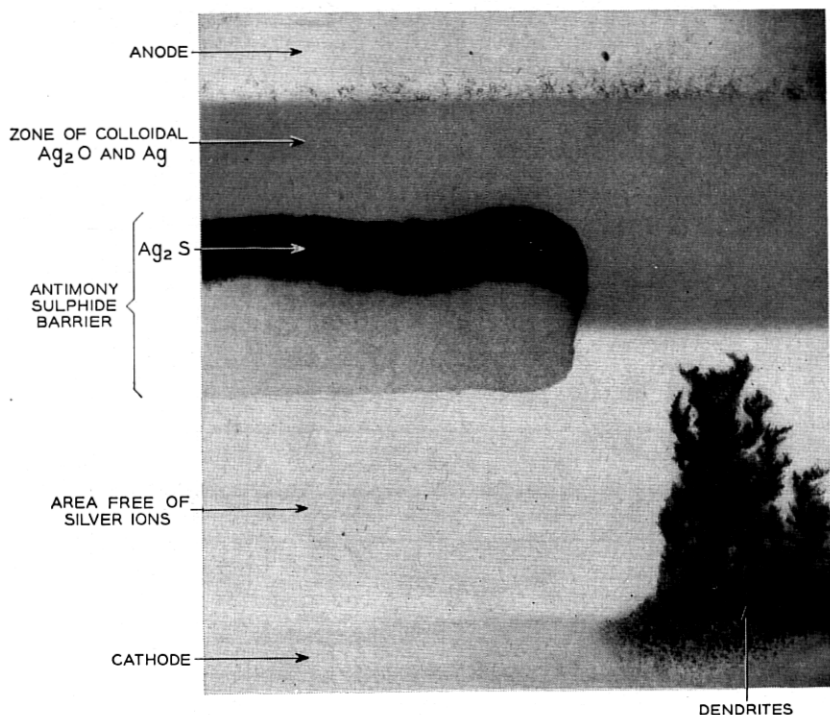


Fig. 18 — Silver migration in CS&S paper with antimony sulfide as barrier, 98 per cent R.H., 45 volts.

when introduced into paper cause the silver to precipitate in the colloidal form in the immediate vicinity of the anode, no dendrites appearing at the cathode until the reducing agent is exhausted. The higher organic acids such as stearic, oleic, and palmitic, appear to have some retarding effect through formation of the almost insoluble silver salts. Benzidine and even egg albumin ties up the silver ions through formation of insoluble complexes. Perhaps the most promising of the precipitating agents, however, is antimony trisulphide,  $\text{Sb}_2\text{S}_3$ . When properly introduced, this compound is quite inert to all but silver and a few other heavy metal ions. It is very insoluble and adds very little conductivity to the paper, yet it precipitates silver ion quantitatively as silver sulphide.

Fig. 18 shows graphically the action of the antimony sulphide. A piece of CS&S No. 598 paper was subjected to silver migration at 45 volts, 98 per cent R.H. Across about two thirds of the paper, a band of antimony sulphide was introduced. Where the silver ions encountered this



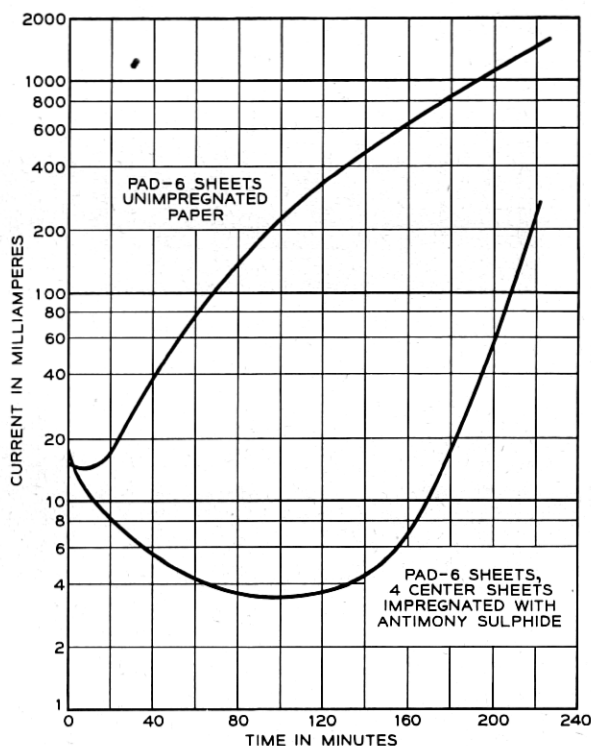


FIG. 19 — Comparison of antimony sulfide impregnated and unimpregnated paper pads.

zone, black silver sulphide was precipitated, none escaping through to the cathode, hence no dendritic growth opposite the band. Where the band is not interposed, the silver ions move freely in the field to give rise to the usual dendritic outgrowth from the cathode. Antimony sulphide is introduced into the paper as the soluble sodium sulphantimoniate. From this, antimony sulphide is precipitated by immersing the dried paper in dilute acetic acid, then the paper is washed free of sodium acetate in running, distilled water.

Fig. 19 shows current-time curves for a 4 square inch pad containing six CS&S No. 598 sheets, the four center ones heavily impregnated with  $\text{Sb}_2\text{S}_3$ . These were first moistened, then placed under 40,000 pounds pressure between the silver electrode platens. A comparison run was made using six unimpregnated papers. This is, of course, a highly accelerated test in which conditions were chosen to favor maximum silver migration. The retardation by the  $\text{Sb}_2\text{S}_3$ , is clearly evident and under

practical conditions it could probably be made to increase the insulation life several fold.

### *Behavior of Inorganic Surfaces*

Brief mention has been made of silver migration on materials such as glass and mica. Evidence has been given in Fig. 7 that surface migration can occur on these materials at high humidities. Ceramics, which are relatively free from water soluble impurities such as high purity alumina and steatite and which possess low surface leakage at high humidity, exhibit migration only at humidities near 100 per cent. It was considered desirable to learn whether migration would occur on a highly insoluble, inert surface such as quartz. A fused quartz plate lightly sandblasted was clamped between silver electrodes in 98–100 per cent

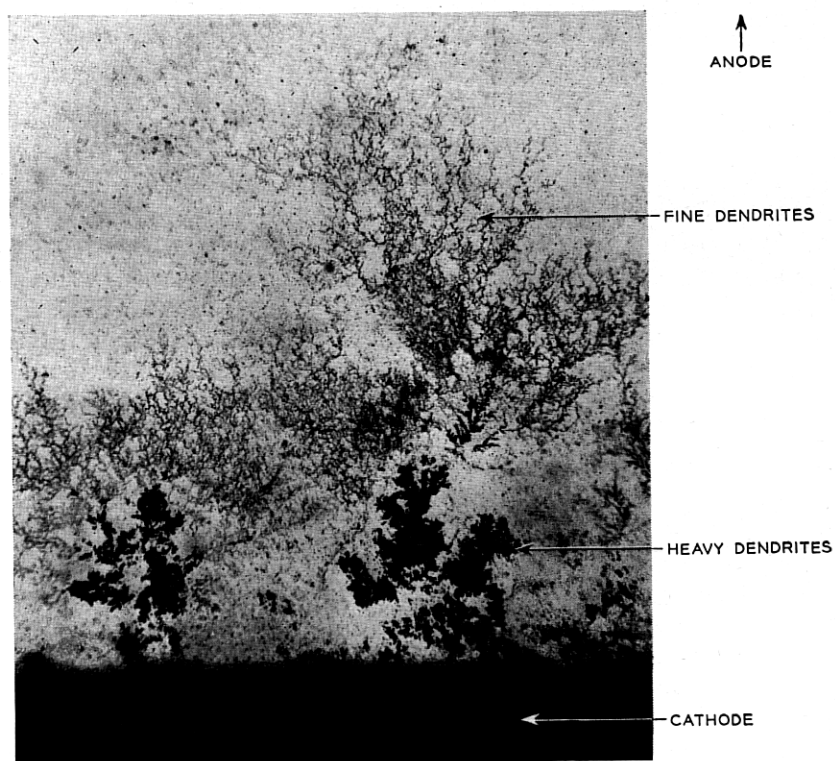


FIG. 20 — Silver migration on quartz plate. Photographed by transmitted light, 100 magnifications, 1500 hours, 98 per cent R.H., 45 volts,  $\frac{1}{2}$ " interelectrode spacing.

relative humidity at 45 volts. After 1,500 hours, dendritic growths were just visible at the cathode to the unaided eye. The anodic area was practically clear except at the points of contact where a slight brownish stain was visible. Fig. 20 shows an area from the cathode outward, viewed in transmitted light at about 100 magnifications. Short, heavy dendrites are seen growing out of the cathode, after which the paths fan out to form a delicate web reaching toward the anode. This experiment, more than any other, tends to show that the only requirement for the migration, given silver and potential, is an adsorbed water layer. Some concern has been expressed regarding the possibility of migration in silvered mica capacitors. Laboratory tests of the open capacitor indicate no migration over the mica when the relative humidity is held below approximately 1 per cent and only slight migration occurs at 90 per cent. When enclosed in a Bakelite housing, however, no migration was observed under these conditions. There is some indication that the Bakelite resin in the assembled unit gives off vapors which exercise an inhibiting action on the mica surface.

#### SUMMARY AND CONCLUSIONS

Silver migration is a possibility which must be considered whenever silver conductors, under dc potential, are separated by insulating materials capable of adsorbing moisture. Therefore, silver should be used with great caution when the conditions discussed herein are present and then only after careful testing to insure that the specific application is safe. In porous or fibrous materials, migration tends to follow the pore or fiber surface and may occur in paths *through* such materials. In non-porous materials, migration is restricted to the surface. The process is primarily electrolytic, involving anodic solution of silver in adsorbed water films with formation of silver oxide in the anodic area. The oxide is non-passivating and appreciably soluble so that silver ions are free to migrate to the cathode. There they are discharged to form metallic dendritic outgrowths which eventually may bridge the anode-cathode space. Electrolytic conduction then gives way to metallic conduction and insulation breakdown may occur. In addition to the cathodic reduction process, silver deposits of a colloidal character may result from chemical reduction either of the oxide in the anode area or of silver ions at any point between anode and cathode.

Ordinarily the colloidal deposits account for little of the observed conductivity, the metallic dendrites constituting the main leakage paths. Where migration is confined to a surface, however, and chemical or

photochemical reduction is intense, the colloidal deposit may attain a density sufficient to conduct appreciably.

The combination of properties leading to migration appear to be found only in silver. There is no evidence that migration occurs with other metals under practical conditions.

No completely effective treatment for silver migration has been devised for application to affected equipment in service outside of replacement of the insulator, where this is possible.

As to the improvement of materials for new equipment, there is reason to expect that something can be accomplished, now that the character of the migration process is known. One possibility is the provision of more effective resin barriers in impregnated fibrous materials. Another possibility is the incorporation of agents which reduce or precipitate the silver ions before these reach the cathodic area.

#### ACKNOWLEDGMENTS

The problem of silver migration has received attention from a considerable number of people in the Laboratories, the A. T. & T. Co., and the Operating Companies during the past fifteen years. A background of experience and opinion thus has been built up, from which the authors have drawn freely. Specifically, the authors wish to acknowledge their indebtedness to J. M. Wilson for his numerous contributions to the field and laboratory evaluation of the migration process and to J. M. A. de Bruyne for his laboratory studies of migration in controlled humidity.

