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Project Whirlwind
Servomechanisms Laboratory
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SUBJECT: ELECTROLYTIC CORROSION AS A POSSIBLE FUTURE SOURCE OF TROUBLE
AFFECTING WWI RELIABILITY

To: 6345 Engineers

From: J. S. Hanson

Date: June 25, 1951

Abstract: On the basis of references in the literature and on the writer's past experiences with troublesome failures of protective electrical equipment due to electrolytic corrosion, this type of corrosion has been shown to be by far the major cause of electrical relay failure. Advanced stages of corrosion recently found in equipment associated with WWI indicates that this phenomenon could be a possible future source of trouble affecting WWI reliability, especially where relays and high voltage power transformers are concerned.

Electrolytic corrosion involves the chemical reaction of copper of the windings with the hydrolysis products of cellulose insulations in the presence of a positive d-c potential and almost negligible amounts of moisture. To eliminate or avoid corrosion it is recommended that: a) the windings of existing relay installations be at negative d-c potentials with respect to any cellulose-based insulation in immediate contact with the windings, b) coils of new or future relay installations contain only cellulose acetate insulation and coverings, and c) the atmosphere contained in hermetically sealed relays consist of only inert gases that are not dissociated into corrosive products by contact arcing.

Past experience with electrolytic corrosion problems involving protective electrical equipment in continuous operation for long periods of time at positive d-c potentials has led to an investigation of this phenomenon as a possible future source of trouble affecting WWI reliability, especially where relays and high-voltage rectifier power transformers are concerned. Since some cases of electrolytic corrosion have already been found in equipment more or less directly associated with WWI, the writer believes that the problem can best be brought to the attention of the engineering staff by

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citing typical examples of the phenomenon and by presenting a brief review of references in the literature.

I. Typical Examples of Electrolytic Corrosion

The first instance cited concerns coil failure of a telephone-type relay in a photo cell unit guarding the cooling water supply for a large underground power transformer. The relay coil was connected in the plate circuit of a vacuum tube at a potential of approximately +150 volts above ground and consisted of a conventional insulated iron core with vulcanized fibre end washers, wound with 50,000 turns or more of #40 A.W.G. enameled copper wire and covered with cotton yarn. A replacement relay would not be available for at least a week, and the transformer could not be deprived of cooling water protection for this length of time under any circumstances, so rewinding was necessary.

In unwinding the old coil, it was found that in each place where the end turns of the layers of wire touched the fibre end washers, the copper had been completely consumed by corrosion, and all that remained were numerous circular paths of white powder adhering to the inner surface of the fibre washer. The powder was analyzed chemically and found to be copper carbonate, an end product of the reaction of carbon dioxide in the transformer vault with the original copper salts resulting from the corrosion process. Relative humidity and ambient temperature in the vault were ideal for such corrosion to take place, although the process frequently occurs even when conditions are supposedly extremely unfavorable, as will be shown.

The second case, an excellent example of an advanced stage of electrolytic corrosion, came to light quite unexpectedly while the writer was disassembling a shorted high-voltage rectifier power transformer removed from a Sylvania P-5 Synchroscope. The transformer was manufactured by the Palmer Electric and Manufacturing Company, Wakefield, Massachusetts, and rectifier circuits involved are shown in Figure 1. Although breakdown of the insulation on high voltage winding S-7 was the immediate cause of failure and not electrolytic corrosion, large pits resulting from the latter were found on the underside of the entire length of filament winding S-6. This winding was at an average d-c potential of +1500 volts with respect to high-voltage winding S-7 which was immediately underneath but insulated from it by four layers of 0.012" varnished cambric followed by two layers of 0.005" kraft paper, as shown in Fig. 2. Corrosion pits were formed wherever the filament winding contacted the kraft paper.

An identical filament winding (S-5) of the same wire (in all probabilities from the same original spool) wound alongside S-6 as shown, on top of the same piece of kraft paper and over the same outer layer of the high-voltage winding, showed not the slightest trace of a corrosion pit.

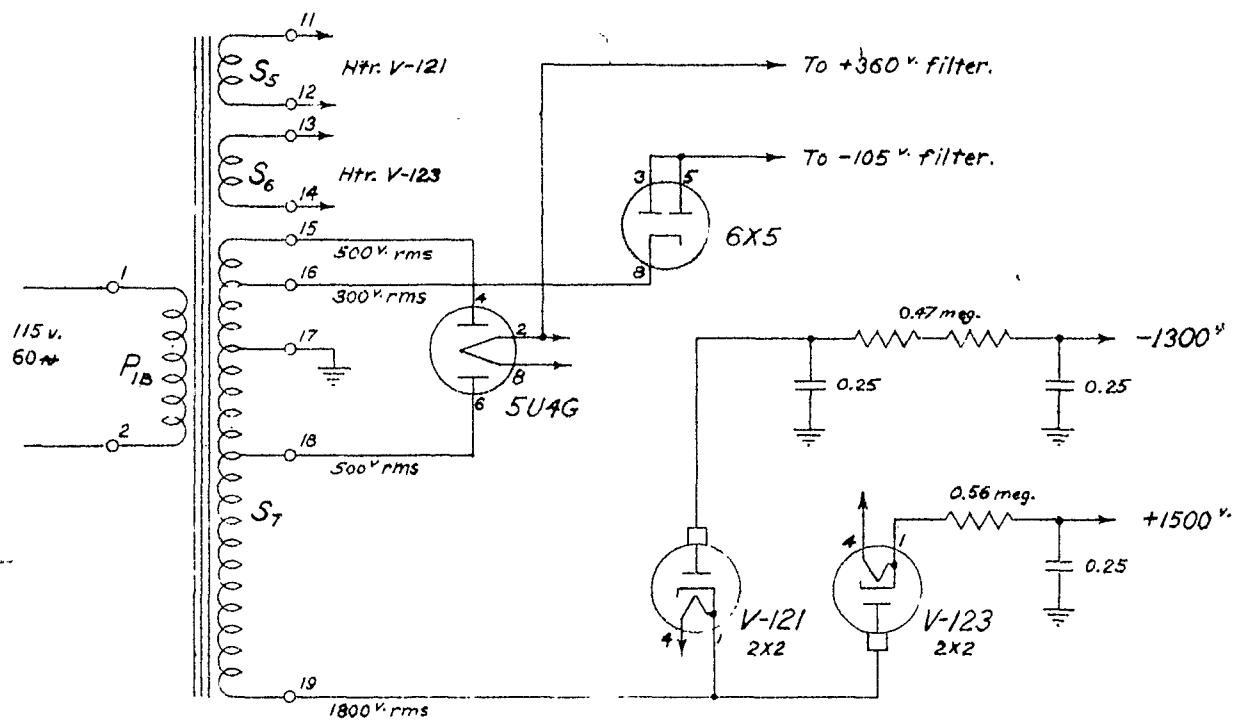


FIG 1. P-5 SCOPE TRANSFORMER WINDINGS AND H.V. RECTIFIER CIRCUITS INVOLVED IN TYPICAL EXAMPLE OF ELECTROLYTIC CORROSION.

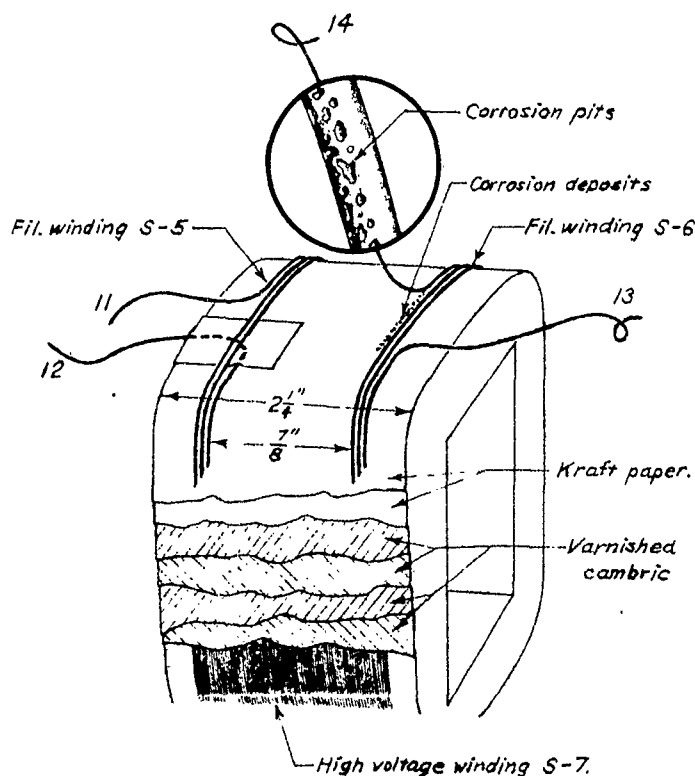


FIG 2. WINDING AND INSULATION DETAILS OF P-5 SCOPE TRANSFORMER.

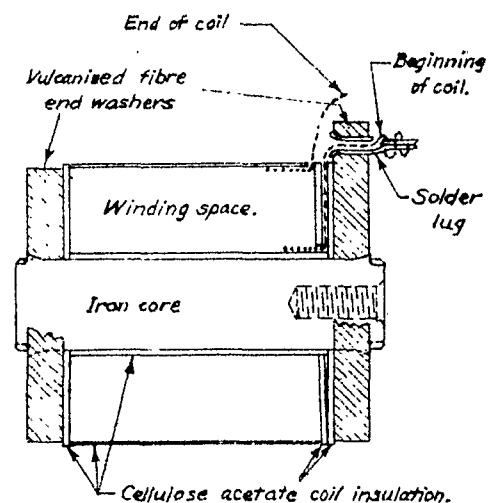


FIG 3. CORROSION-PROOF RELAY COIL WITH CELLULOSE ACETATE INSULATION.

This filament winding was electrically connected to the high-voltage end of winding S-7, so that regardless of the instantaneous a-c potentials involved, its average d-c potential with respect to the high-voltage winding was zero. A strikingly effective photographic comparison of samples of both filament windings is shown in Figure 4.

Samples of the kraft paper insulation which had been in direct contact with the two filament windings are shown at approximately the same magnification in Figure 5. In the upper photo, the dark elongated area inside the rectangle is a section of the enamel from the uncorroded wire which adhered to the varnish impregnation of the kraft paper during unwinding. The glossy surface was completely free of all traces of corrosion. Effective side lighting in the lower photo shows the small "mountains" of copper salts deposited in positions corresponding to the pits in the overlying wire and of considerably lighter color than the underlying insulation or the surrounding pieces of enamel adhering thereto.

That this corrosion was able to proceed for a year or more under apparently unfavorable conditions, with the windings supposedly baked, varnish impregnated, asphalt potted, and hermetically sealed in a metal case will be demonstrated in Section V, page 10.

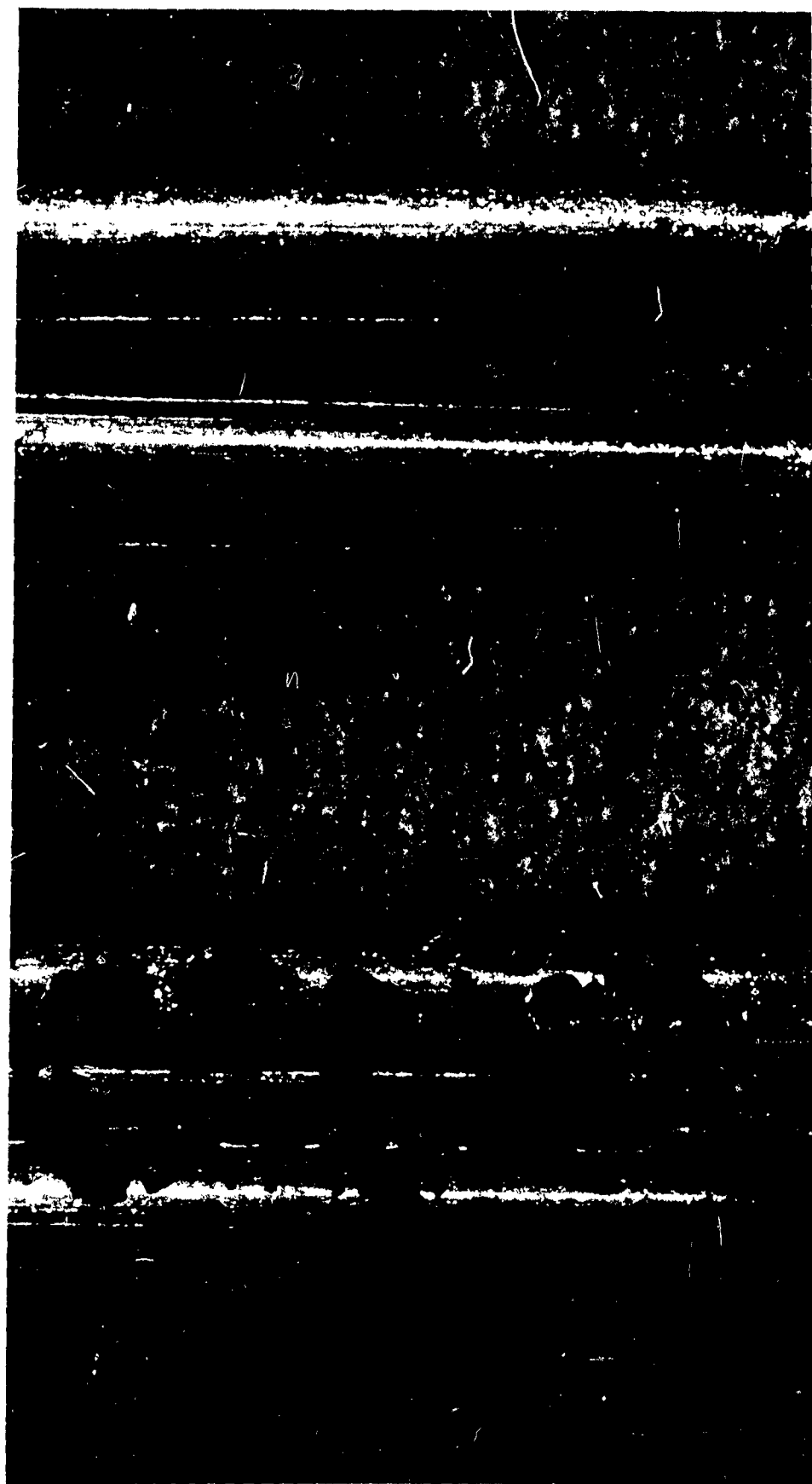
II. Original Concepts of Electrolytic Corrosion^{1,2,6}

After electrolytic corrosion was recognized as a definite source of failure, it was first believed that free acids in insulating materials contacting the wire were responsible. As various investigations progressed it was soon realized that not only materials with acidic reactions but those containing bases or salts were also guilty.

It was next reasoned that the amount of corrosion exhibited by an insulating material during a certain estimated period, hence its rate of corrosion, was somehow related to the conductance of the material or inversely proportional to the insulation resistance (specific resistance) of the material, but there were still some materials with much lower insulation resistance which showed very little corrosion.

Moisture absorption or adsorption of materials was next supposed as the primary factor in corrosion where surrounding humidity was high and the corrosion obviously most serious, but again, some materials with high moisture absorption capacity exhibited much less corrosion.

Each of these suppositions was subsequently refuted as careful investigations eliminated them one by one, since it was now recognized that electrolytic corrosion was indeed the major cause of equipment failure erroneously attributed to other causes, and that it was a problem demanding an immediate solution. Since methods of minimizing or completely avoiding effects depend on: a) an understanding of the corrosive properties of supposedly "innocent" materials under the right conditions, b) the causes of corrosion, and c) the mechanism of corrosion involving copper windings, these topics will be considered first.



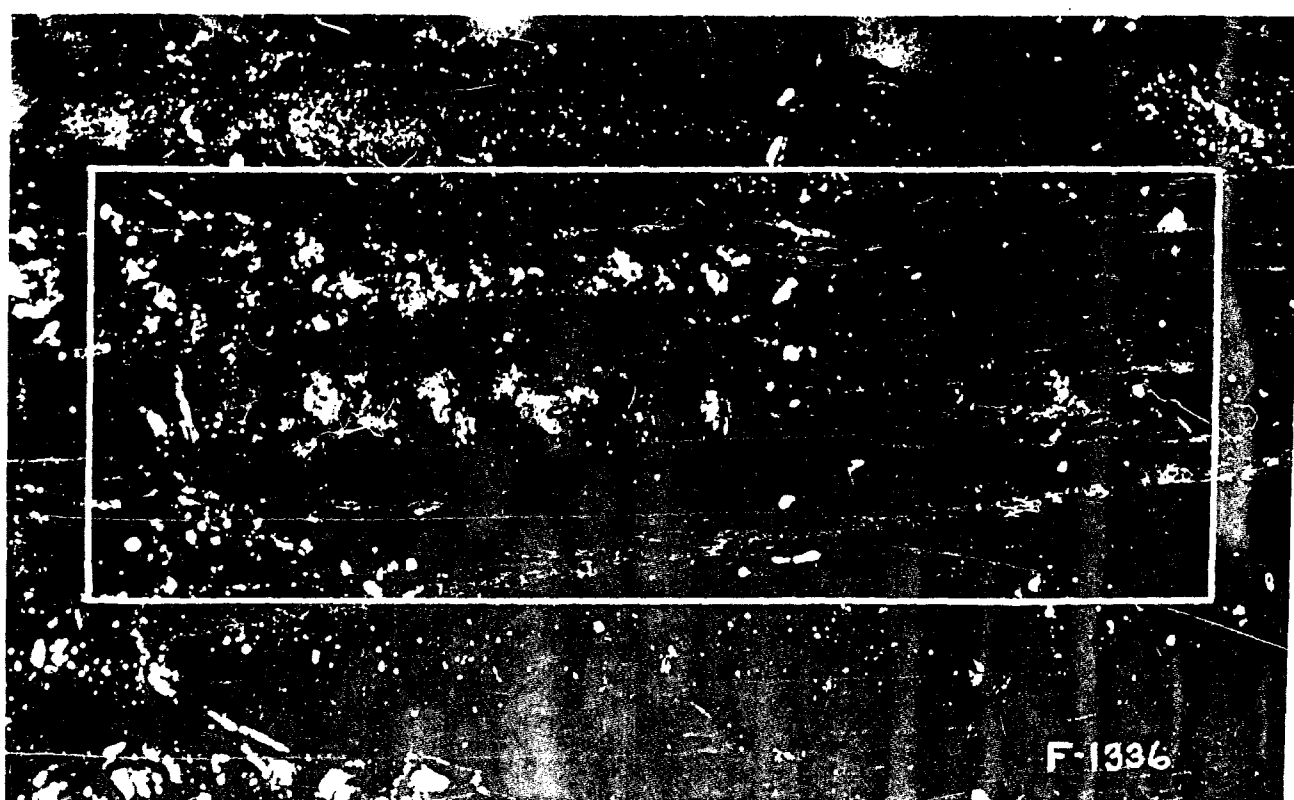
COMPARISON OF INTACT AND PITTED SAMPLES OF TRANSFORMER
(0.040" DIAM.) SHOWING ADVANCED STAGE OF ELECTROLYTIC
FIG. 4

A-50093



COMPARISON OF INTACT AND PITTED SAMPLES OF TRANSFORMER FILAMENT WINDINGS
(0.040" DIAM.) SHOWING ADVANCED STAGE OF ELECTROLYTIC CORROSION.

FIG. 4



COMPARISON OF FILAMENT WINDING INSULATION SHOWING DEPOSITS OF COPPER
SALTS (LOWER PHOTO) RESULTING FROM ELECTROLYTIC CORROSION.

FIG. 5

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III. Corrosive Properties of Insulating Materials²

Various major classes of commonly used insulating materials exhibit corrosion effects under favorable conditions of humidity, d-c potential, and ambient temperature.

A. Adhesives

1. Glues, even highly purified, are highly corrosive, and should not be used for electrical purposes under any conditions, since they hydrolyze* very rapidly under ambient conditions of high humidity and elevated temperatures, producing organic acids which are a major cause of corrosion.
2. "Dialyzed" glues, even though substantially electrolyte-free at first, show no improvement whatever because the glues themselves are sources of electrolytes, as just shown.
3. Mucilage, a gelatinous plant extract containing complex carbohydrates, with or without starch bases, is similar to glue in its hydrolyzing and corrosive properties, hence should also be avoided.
4. Rubber-resin, and even the common adhesive tape coatings of rubber, rosin, and zinc oxide, have no corrosive properties whatever, even after accelerated aging tests equivalent to five years of normal life. This class of adhesives contains abietic acid which is so weak and difficultly soluble in water that its acidic properties, even under the most favorable conditions for corrosion, are negligible.
5. Resin-based adhesives, commonly known as "sticking varnishes" in the electrical manufacturing trades, are likewise non-corrosive, but are not as instantly effective as the rubber-resin adhesive mentioned above, in that they require a partial drying period before adhesive properties become appreciable.

* Hydrolysis is a chemical decomposition process involving the addition of hydroxyl ions (OH^-) from moisture present in the material.

B. Insulating Materials, Tape Backings, etc.

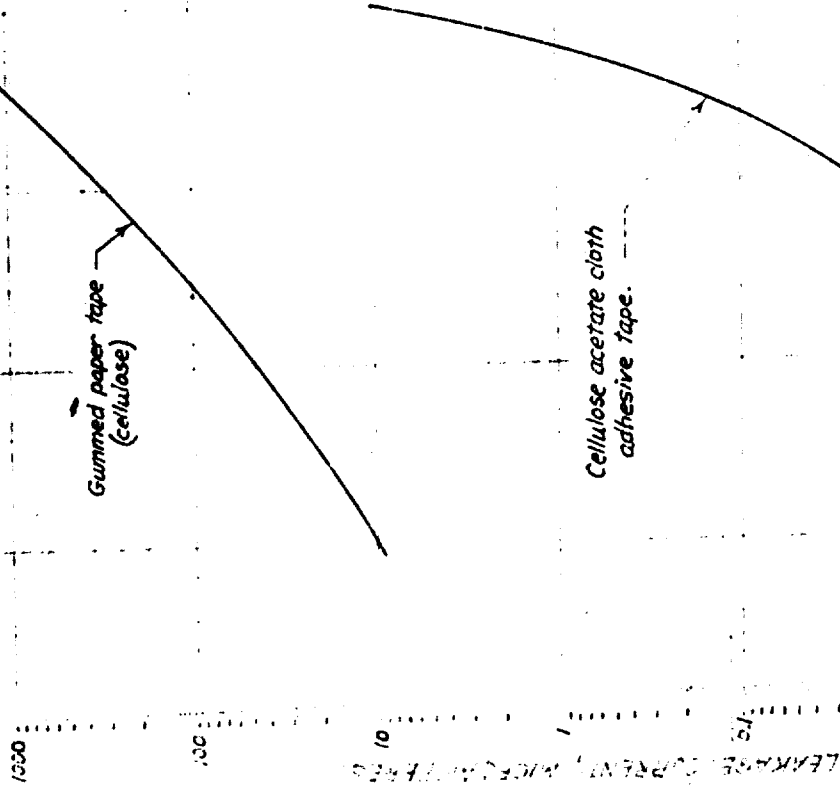
1. Cellulose-based electrical insulating materials, such as paper, fibre board, vulcanized fibre (horn fibre, leatheroid), cotton cloth, linen, viscose rayon, cellulose film (cellophane), and wood fibre are all corrosive materials in the presence of d-c potentials and slight traces of moisture.
2. Silk and wool are also corrosive, but wool (also a protein fibre like cellulose) is considerably better than either silk or cellulose, even though its water absorption capacity is much higher.
3. Bakelite, which contains impregnated cellulose in the form of either linen, cotton, or paper, has been shown to be corrosive³ wherever the cellulose is in immediate contact with current carrying conductors.
4. Chemical compounds of cellulose such as cellulose acetate and cellulose nitrate (celluloid), rubber compounds, and synthetic resins such as polystyrene (plexiglass), methacrylates (lucite), and vinyl plastics are all free from corrosive effects on copper. Cellulose acetate especially, in both sheet and woven cloth forms, shows no tendency toward copper corrosion even after the most exhaustive tests. According to Stephens and Gehrenbeck, "there is every indication that a fine copper wire in contact with cellulose acetate will last as long as one freely suspended in air."

In Figure 6, a comparison of the relative leakage currents of two common insulating materials, gummed paper tape and cellulose acetate cloth adhesive tape, shows the effect of varying combinations of the aforementioned hydrolysis, leakage resistance, and moisture absorption properties. Since the individual effect of each of these properties is difficult to determine, leakage resistance is not a dependable measure of insulation quality where favorable conditions for corrosion exist.

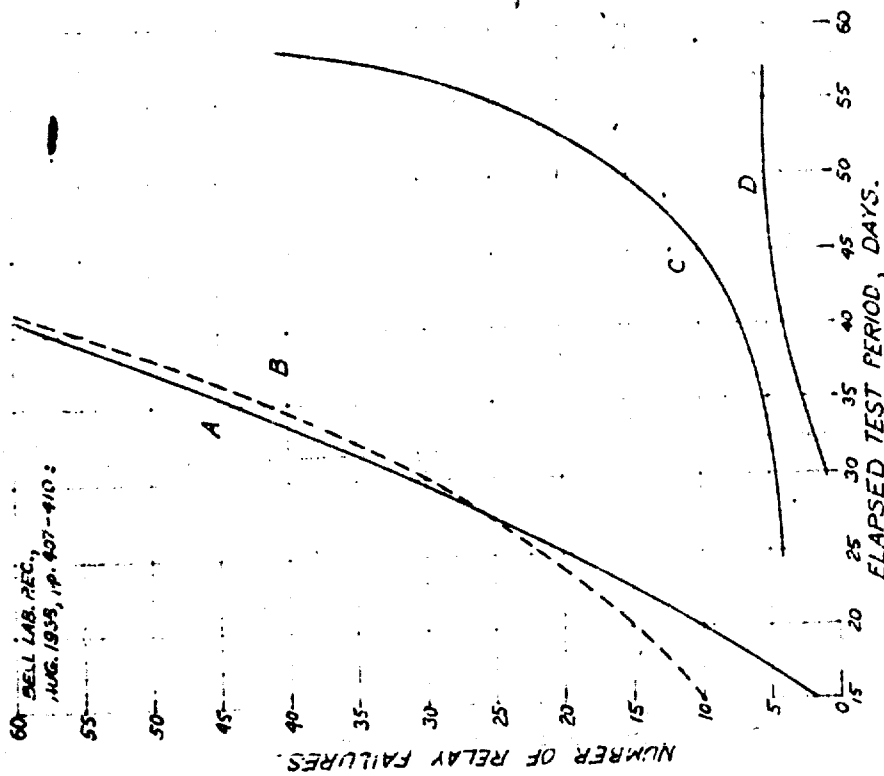
IV. Causes of Corrosion^{1,2,6}

Paper, cotton or linen cloth, viscose rayons, cellophane, and wood fibre, in the presence of a d-c potential and slight traces of moisture have all exhibited marked corrosion effects. In investigating corrosion effects of various kinds of paper insulation, for example, water extracts of all kinds of paper ranging from the cheapest wrapping paper to the highest quality ash-free chemical filter paper of the highly purified alpha-cellulose type varied widely in pH content and electrolytic conductivity. Low grade papers caused very bad corrosion, but there was not enough significant difference between the worst and best quality papers

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- A- Mixed paper core cover, interwinding insulation, and outer cotton yarn sewing.
- B- Same, but impregnated.
- C- Cellulose acetate yarn core and cotton covers, stored paper interwinding insulation.
- D- All coil insulation of cellulose acetate sheet.

85 90 95 100
% RELATIVE HUMIDITY

FIG. 7. EFFECT OF HUMIDITY ON LIFE EXPECTANCY OF RELAY.

to warrant any conclusion other than that cellulose itself was to blame. Cotton fabrics yielded identical results.

One effect of corrosion observed was the chemical oxidation of cellulose in the presence of moisture at the anodic surface of a pair of fine platinum wires 3/16" apart, producing water-soluble organic acids. The entire area of the material involved in the immediate vicinity of the platinum electrodes acquired reducing properties, indicating either hydration or oxidation. Free acid was present only along the thin line where the positive electrode contacted the material. This acid combines with copper to form a green corrosion product.

Electrochemical oxidation is readily demonstrated by means of an oxidation cell containing a ground-up suspension of neutral cellulose fibre in distilled water. Passage of an electric current through the cell produces large quantities of complex water-soluble organic acids.

The above effects are completely independent of the presence or absence of minute traces of electrolytes in the original samples, therefore there is no point in extreme purification, or even mild purification of papers or cloths, hence the fallacy of specifying "acid-free" insulating papers.

Since the development of corrosive properties in protein materials could be almost completely due to hydrolysis and not oxidation, one can immediately specify insulating materials with the following chemical characteristics:

- a) inherently non-electrolytic
- b) resistant to oxidation or hydrolysis (e.g., cellulose ethers, esters, nitrates, or acetates)
- c) if not resistant to oxidation or hydrolysis, then the material (rubber compounds, for example) must yield only non-electrolytic decomposition products.

From b), the best solution to the problem is to replace the hydroxyl components of the cellulose materials with ethers, esters, nitrates, or acetates, the last mentioned being the most practical and economical.

V. Mechanism of Copper Corrosion²

For corrosion to exist, two prerequisites are necessary:

- a) oxidation conditions at the surface of the copper, and b) availability of a negative ion. The oxidation of metallic copper to cupric ion can be written as $\text{Cu} + 2\text{e}^- \rightarrow \text{Cu}^{++}$ and the corrosion process then becomes $\text{Cu}^{++} + 2\text{A}^- \rightarrow \text{Cu A}_2$ where A^- is the needed negative ion, the corrosion compound being deposited on the insulation at the positive wire as long as there is a path through which the ions can move, namely that supplied by

water in the cellulose itself. Note that there is always a minute flow of current associated with this process which may take anywhere from a week to even years to completely consume the wire at a point. Even in low humidities, or virtual absence of free water in the material, corrosion can take place even at a very slow rate. This is readily demonstrated by the existence of electrolytic corrosion in the transformer of Example 2, page 2, even with the windings supposedly baked, varnish impregnated, and surrounded by an asphalt potting compound in a hermetically sealed metal case.

VI. Methods of Protection Against Corrosion

Tests and investigations have shown that the major cause of relay coil failure is electrolytic corrosion. This does not include a small percentage of other failures of either electrical or mechanical nature involving partially shorted coils, open-circuited windings resulting from continuous heating and cooling cycles, grounded windings resulting from insulation failure, or mechanical failures such as welded contacts or sticking armatures.

Obviously, if all cellulose-based insulating materials and adhesives containing glue or other hydrolyzing substances are eliminated from relay coils of fine wire energized for long periods of time at positive d-c potentials, relay life expectancy is without limit where corrosion elimination is concerned, as shown in Figure 7, page 9.

If cellulose insulating material must be used for economical reasons, it must be protected so that the copper can never come into contact with the material itself. For example, relays such as used in the punched tape and typewriter equipment associated with WWI depend on vulcanized fibre washers staked in place for mechanical support of the fine copper wire windings of the relay coil as shown in Figure 3, page 3. A thin washer of cellulose acetate film prevents the wire from coming in contact with the fibre. The protective covering for the coil, as well as coil insulation, consists of a thin, adhesive-coated cellulose acetate film. Practically all telephone-type relays, stepping switches, and ringing mechanisms manufactured within the past ten years utilize this type of coil construction.

If in a particular relay installation, coil insulation is not of cellulose acetate, any tendency toward electrolytic corrosion can be completely eliminated by reinstalling the relay in the negative side of the d-c source of voltage where circuit conditions permit. However, if bias requirements for a vacuum-tube-actuated relay, for example, prohibit insertion of the relay coil in the cathode circuit of the tube, corrosion can still be eliminated by leaving the coil in its initial location in the plate circuit of the tube, but with the relay frame insulated from ground and connected to the +B supply potential. In various other installations, corrosion may be minimized in the case of relays with comparatively low coil voltage ratings by grounding the inner or starting end of the coil, so that except for short periods when the relay is energized, the coil has no d-c potential on the windings. This last method is ineffective in eliminating corrosion if the relay is energized for long periods of time.

VII. Other Corrosion Effects

It is considered expedient to mention a few other forms of corrosion occasionally encountered in relay installations which might be considered as factors affecting WWI reliability.

At the suggestion of B.W. Erickson of the General Electric Company, mica and asphalt compounds were subjected to corrosion tests by Gehrenbeck, in which 90 volts d-c was placed on two #32 bare copper wires held 3/16" apart on the curved surface of the insulation samples by a slight tension. No corrosion effects were discernible even after long periods at 100% R.H. and 40°C ambient, whereas coils insulated the top grade cellulose seldom lasted more than ten days. He found, however, that wherever the positive copper wire was allowed to contact the edge of a mica sample and not a flat unbroken surface, noticeable corrosion effects were caused by traces of electrolytes between mica laminae. For this reason, the writer does not advocate mica tape insulation as a solution because of the large number of edges presented to the windings.

A corrosion effect involving a telephone relay contact spring and a bakelite backstop was attributed³ to the action of the cellulose fibre of the grounded bakelite coil washer on the contact spring which was energized at +48 volts d-c in abnormal heat and humidity. Replacement of the bakelite washer with a molded bakelite part eliminated the corrosion.

As early as 1938, Garvin¹ had suggested cellulose acetate as a material entirely free of corrosive effects, even in the presence of slight amounts of moisture, although his diagnosis of the cause of corrosion did not reveal the true nature of the phenomenon.

As a final example,⁴ a cycling test was made on a relay "protected" against dust and atmosphere corrosion by a glass cover and rubber gasket, the test consisting of deenergizing the relay once every 4 seconds to interrupt three 60-cycle a-c loads of 220 volts, 3 amperes, 25% p.f. each, and one d-c load of 70 volts, 1 ampere. After only 4000 cycles of operation, contact arcs reacting with the air inside the cover produced a slight nitric acid atmosphere. Anhydrous copper nitrate was formed on the beryllium copper contact springs at 30,000 cycles, amorphous zinc nitrate zinc plating at 50,000 cycles, and the atmosphere became strongly acidic at 63,000 cycles. At 90,000 cycles, ozone concentration became high enough to oxidize surfaces of silver contacts, hydration of the copper nitrate at 92,000 cycles was indicated by appearance of green coloring, and coil insulation and gasket material began to deteriorate at 800,000 cycles. At 850,000 cycles the zinc plating was completely consumed, exposed iron surfaces were completely rusted, and corrosion products began to pile up in the bottom of the glass cover. The cumulative chemical reaction resulting from the arcing was given as:

nitrogen + oxygen $\rightarrow$ nitric oxide (gas)

nitric oxide + oxygen $\rightarrow$ nitrogen peroxide

nitrogen peroxide + water vapor $\rightarrow$ nitric acid + nitric oxide

Four 1/4" diameter holes drilled in the base of another identical relay operating under the same load conditions prevented any trace of corrosion even after one million cycles.

VIII. Conclusions

In order to avoid any of the foregoing corrosion troubles, it is recommended that relay installations satisfy the following: a) the windings of existing relays be at a negative d-c potential with respect to any cellulose-based insulation in immediate contact with the windings, b) coils of new or future relay installations contain only cellulose acetate insulation and covering, and c) the atmosphere contained in hermetically sealed relays consist only of inert gases that do not react with contact arcs to form corrosive products.

No attempt has been made in this report to deal with the more familiar relay troubles such as mechanical failure, contact pitting and burning, and dust accumulation on contacts of relays improperly mounted. The discussion has been limited to corrosion effects of electrolytic or atmospheric nature.

IX. Bibliography

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Drawings included:

pg. 3	Fig. 1, 2, and 3:	SA-50054
pg. 5	Fig. 4:	A-50093
pg. 6	Fig. 5:	A-50094
pg. 9	Fig. 6 and 7:	SA-50050-1