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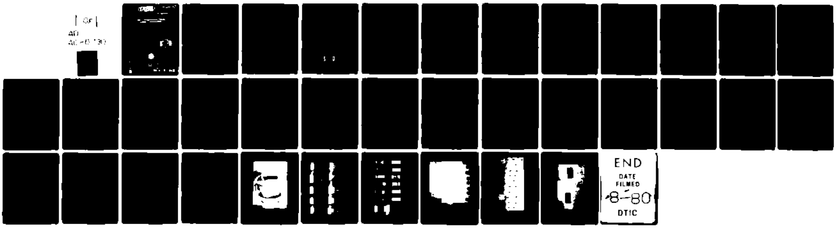

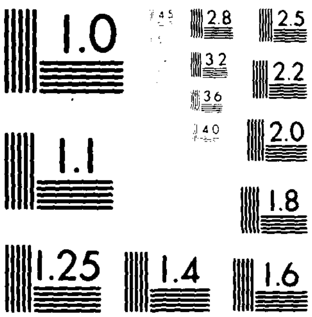

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Electrical disturbances caused by the formation of corrosion products on computer contacts is a serious problem, especially in older contacts containing a tarnish-prone silver layer under gold plating. The efficacy of a number of corrosion preventative organic fluids in preventing corrosion in sulfide-bearing atmospheres has been evaluated, in conjunction with a chromating process for the same purpose. Studies were made both with connectors and with silver. A statistical treatment applied to visual evaluation clearly identified two organic formulations as effective corrosion

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20. Abstract (Continued)

inhibitors, verifying other observations. These fluids were as effective as chromating alone, but an additional measure of protection was afforded by the combination of chromate/organic fluid.

CONTENTS

STUDIES OF CORROSION PREVENTION OF MARDAN CONNECTORS BY ORGANIC COATINGS

I. Introduction

Female connectors in the MARDAN computers experience failure in service that has been shown (1,2,3) to be accompanied by the formation of an insulating layer of corrosion. The corrosion products appearing on the outer gold coating of the female connectors consist in part of sulfides of the silver intermediate layer in the old-technology connectors in service (4). Wear or other discontinuity in the gold coating exposes the Ag which reacts with sulfur to form Ag_2S (5). Chromating connectors after cleaning and detarnishing them affords a moderate level of protection from subsequent corrosion. Presently, the chromated connectors are devoid of lubricant.

Organic films for corrosion protection of electronics connectors have been described (6,7). Dielectric materials introduced into a connector for this purpose must be in an extremely thin continuous film. Such films could be used to replace or enhance the protection afforded by the chromate layer. Organic coatings have the advantage of easier application during emergency refurbishing, as well as providing lubrication to prevent contact wear.

Previous studies (8,9) had tentatively identified one organic fluid, MIL-C-81309, to be used in combination with chromating as a candidate system for serious evaluation. Long-term life tests of this compound are underway at Autonetics (10). NRL has been tasked with the objectives of identifying additional organic film candidates for corrosion protection, evaluating their usefulness, life expectancy, and corrosion resistance both as replacements for and in conjunction with the chromating process.

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Several types of connectors were available for this study. A specially prepared sample lot of new connectors made to conform to the old Au/Ag/Cu technology, hereafter referred to by the acronym (NCOT), were obtained and used in the majority of studies reported here. Other connectors included corroded female connectors removed from actual fleet service, unused female connectors and replacement pins made with current technologies that eliminate the silver layer, and male connectors adapted by Autonetics from printed circuit boards (PCB).

The work here is reported in three sections and followed by a general discussion in Section V. Section II reports studies on NCOT resistance to sulfide corrosion afforded by coatings of the candidate protective fluids with and without the chromate process. The H_2S for this work was provided by a $(NH_4)_2S$ solution. Section III describes a separate set of tests made with pure H_2S gas at elevated temperatures, and Section IV reports studies with electrified connectors.

II. Studies of NCOT Female Connectors in $(NH_4)_2$ Sulfide Atmosphere at Ambient Conditions

A. Materials

Female 86-pin NCOT connectors were obtained from Autonetics. Each was assigned an identification number and sawed into segments having 8 to 14 intact pins. (Pins damaged during cutting were removed prior to testing.)

The sulfide test atmosphere was provided by the vapor from aqueous $(NH_4)_2S$ solutions. Solutions for use were prepared by dilution of a 9% nominal $(NH_4)_2S$ "light" solution (Fisher Scientific Co.). Wet chemical analysis of the $(NH_4)_2S$ using the Hach (11) field test showed the effective H_2S concentration was 1.75 gm per liter. A 1000:1 dilution of this solution yielded the solution for use. It had a light yellow color and a strong odor of H_2S. Drager gas tubes (12) tested the H_2S level generated in the test chamber to be 4 to 50 ppm during the first six hours of experiments. The H_2S dissipated, leaving the solution colorless and H_2S in the test chamber atmosphere undetectable (<0.5 ppm) at the end of a 12-hour study interval.

The candidate fluids for evaluation as corrosion preventatives were chosen on the basis of several considerations. Materials that could be applied as films that would remain fluid were of most interest, as they are expected to remain protective longer by the virtue of their being self-healing. Selected compounds also had to potentially resist thermal and oxidative degradation and to represent a class of potential protective agents. The materials selected for study are described here; their properties and code names are listed in Table I.

MIL-C-81309 had been identified (13) as a commercially available anti-corrosive, water-displacing agent designed for use on electronic equipment. NyeTack Fluids 515 and 518 are commercially available preparations for lubrication and corrosion protection of electrical contacts. NyeTack 517 is an experimental formulation for this purpose (14). Cramolin Blue and Cramolin Red are commercially available corrosion protective fluids for cleaning and lubrication of electrical contacts (15). They are supplied for use either alone or in sequence, and were evaluated in both ways.

MIL-L-81846 is a formulated polyol ester-diester-based lubricant that is specified for precision miniature bearings with long service lives (16). Its proven long-term stability, as well as its formulation enabling us to include the effects of anti-wear and oxidation-inhibiting additives, were the bases for its selection. A polyphenyl ether, 4P3E, was chosen because of its previous use as a lubricant in electronic components (17).

Sodium hexametaphosphate is a corrosion-preventive compound that is effective on surfaces in contact with aqueous media (18). It was the only solid compound evaluated. It was able to be applied as a fluid from a dilute aqueous solution.

A fluoropolymer solution used for forming protective oil-resistant barrier films having low surface energy and low friction was tested. Its ability to form thin, continuous non-wettable polymer films that show virtually no degradation in long years of service life (19) was a major consideration for its inclusion. While the dried polymer film is a solid, self-healing might occur with a melting-type reorganization of the polymer's long side chains that is known to occur near room temperature (20). A representative of the perfluorinated lubricants was the oil base of Bray 3L-38RP (21). This perfluoroalkyl ether fluid was chosen for its inertness, lack of chemical reactivity and extremely low vapor pressure, all of which provide long-term chemical stability sufficient for space applications.

A representative silicone dielectric gel, MIL-S-8660B, was selected. The inertness and low reactivity of silicones are supplemented by their pronounced tendency to creep over metal surfaces which might enhance the self-healing in a thin film.

B. Experimental Methods

Connector preparation tests were carried out on NCOT connectors that were as-received (AR), washed (W), detarnished (D), chromated after being washed and detarnished (C), and scratched (S) either before chromating (SC) or after chromating (CS). The connector sections to be used in as-received (AR) tests were rinsed with distilled water and allowed to dry. Test conditions and combinations are listed in Table II.

Cleaning, detarnishing, and chromating procedures were carried out according to NAVORD 0245273 (22). Washed connectors (W) were soaked in warm Turco detergent for three hours, cleaned ultrasonically five minutes and/or with a brush, rinsed with distilled H_2O, and after a final rinse with warm distilled H_2O, air-dried. After detarnishing with the specified solution, samples were again rinsed with distilled water and air-dried for further use as samples labeled D, or subjected to the chromate treatment. Samples labeled C were chromated with Kenvert MOD-3. Newly chromated samples were held at 60°C for 48 hours, followed by retention at room temperature for at least 24 hours before further handling.

Samples labeled S were deliberately scratched on the front connection to PCB region and back solder lugs of each spring pin; Fig. 1 shows the regions of a connector pin labeled front and back and the locations of test scratches. Scratches were made with a hand-held tungsten carbide scribe. Care was taken to reproduce both the angle of the scribe and the pressure applied. Tests were made on connector sections whose pins had been scratched either prior to chromating (SC) or after being chromated (CS).

Except for 81309, the corrosion-prevention fluids were applied with fresh cotton swabs to all exposed metal surfaces, lightly coating the exposed pins both fronts and backs. After application, any excess fluid was wiped away with a second dry swab to leave a thin, uniform film. MIL-C-81309 was obtained as an aerosol spray (13). Connector sections tested with it were sprayed and the excess drained on filter paper. The pins then were wiped with a dry swab to leave a thin film.

The samples with test fluids were labeled and placed in a desiccator with a measured quantity of the $(NH_4)_2S$ solution at room temperature (25°C). Figure 2 shows a typical test arrangement for NCOT sections. After 12 hours, the ranks of corrosion resistance of both fronts (F) and backs (B) of samples were recorded and the sections were replaced in the chamber with a fresh dose of $(NH_4)_2S$ for a second 12-hour interval. They were ranked again, and replaced for a third 12-hour exposure to $(NH_4)_2S$ that was followed by the third and last ranking.

Studies in the $(NH_4)_2S$ atmosphere were also made on individual spring pins removed from NCOT connectors and from the used connectors. Care was taken to avoid scratching of the pins, as the lower edges and an area just below the dimple in the spring pin are the most likely regions to be damaged during removal. Tarnish formation in these areas was discounted in assessing lubricant effectiveness. Usually, small glass dishes were used as receptacles for individual pins in the test chamber. To test for any effect of contact with glass, some tests were made with individual pins placed in polyethylene containers of similar size and shape as the glass dishes. There were no differences in behavior of pins contacting either glass or polyethylene.

C. Results

The connector sections were ranked for corrosion damage of both fronts and backs after each of the three 12-hour test intervals. For some tests, the damage was so mild at 12 hours that no effective ranking could be established. The curved fronts of the spring pins always appeared to be less affected by $(NH_4)_2S$ exposure than the backs. Examination of the regions of pins that would actually contact the PCB tabs was made by removing pins from the connector after the $(NH_4)_2S$ exposure. These inner regions had tarnished more than the adjacent curved fronts; the corrosion level in these inner regions was more similar to the backs. A typical ranking of the level of corrosion of backs of CS NCOT sections after 36-hour $(NH_4)_2S$ exposure is shown in the photograph of Fig. 3. Because the backs of NCOT sections show the corrosion more noticeably than the fronts, a representative set of connector backs after $(NH_4)_2S$ exposure is shown in Fig. 3. The order of increasing tarnish on the fronts of these samples is the same as that shown for their backs. Rank ordering, supplemented by records of visual detail, was used for all samples.

The visual inspection and rank data indicated some trends, but the raw rank data was difficult to interpret in detail. We were interested in using the data to obtain information to answer a number of questions suggested by the data: (1) Did lubricants on the fronts of connectors yield different rankings than those on the backs? (2) Were there differences in lubricant effectiveness at the several time intervals (implying a change in the relative effectiveness of a lubricant's protection after sulfide exposure)? (3) How did CS and SC connectors differ from each other and from the unscratched AR sections? (4) Would previously studied NCOT connectors behave differently after refurbishing from NCOT connectors first studied? (5) Could we identify on a sound basis the several best candidates, as well as eliminate the poorest ones, and show under which test conditions they were most effective? (6) Last, could we show any global trends if all the data were combined?

To obtain this kind of information, statistical analysis was required. The statistical test used here first calculates the mean rank from all the replicate experiments for any given lubricant in a particular test case. The mean rank is defined as the arithmetic average of the η replicate raw data ranks, i.e.,

$$\text{Mean} = \frac{\sum^{\eta} \text{rank}}{\eta}$$

In this way, a mean rank is generated for each lubricant that was included in a given test mode. This mean rank for each fluid was then tested against the others within a test mode data set in order to determine which mean values were significantly different from each other. For this kind of test, the Duncans t-Test (23) is especially suitable. It mathematically generates the internal error considerations needed to make close comparisons of several means within a data set. The Duncans test was used with each lubricant mean within a given test mode. It compared a lubricant mean rank sequentially against each of the other mean ranks in the data set, and determined whether that lubricant was significantly different from each of the others. Mean ranks that did not differ significantly (here at the confidence limit of $\alpha = 0.05$) were assigned to the same distribution, as indicated by letters in the data tables. Because of the multiple comparison, lubricant mean ranks might be assigned to more than one distribution, in which case that lubricant does not differ from those in all the distributions to which it belongs. The Duncans test thus creates subgroups of lubricants that can be distinguished statistically from each other in their corrosion protection ability. The results of applying Duncans test to the ranked lubricant data are given in Tables 3-6.

Table 3 shows data for ten lubricants from CS and SC experiments and compares data for fronts only and backs only to the combined data. The lubricants are listed in the order of the combined ranking: rank 1 represents best performance. Under the combined data heading, the range of observed experimental rankings from the several tests is given, as is the mean rank value. The sample populations are shown by letters. It can be seen that only the top three candidates fall into the A and B distributions. The next five in the list (distribution C) do not really differ from each other, and some mean values in the C group do not differ from those in the D group. The data for backs of connectors is shown in the center section of Table 3. The top three candidates are in the A distribution, but the third candidate is also related to those in the middle of the list (B and C groups). Several of the rank orders are inverted in the middle of the rank list, but these are still within the same C group, and the outcome for the highest and lowest ranking candidates was not changed. The front data, in the last third of Table 3, shows approximately the same ordering as the overall data, with the top two candidates alone in group A while the others belong to overlapping distributions.

These results show that there are two (perhaps three) candidates that are significantly better than the others. In all three sequences, 81309 is superior and NY 518 is a close second. The NY 515 lubricant is usually third in ranking, but it is not always significantly better than the rest of the lubricants sampled. It also can be seen that the data for fronts and backs are quiet similar, with larger significant overlapping distributions resulting in part from dividing the data into smaller sample populations. The top three candidate rankings were not altered, however, and the similarity of their results suggests that ranking of backs or large exposed areas of connector pins is at least as effective for evaluation purposes as the more difficult rankings of the fronts.

The rank data in each test group were always obtained from sections that had been cut from more than one large connector. Random distributions of the results from individual source connectors gave assurance that rankings were not affected by a source connector.

Table 4 shows the results obtained for analyzing the CS and SC data as a function of $(NH_4)_2S$ exposure time. After both 24 and 36-hour tests, the 81309 and NY 518 are still effective. After 36 hours, the NOLUB control is rated third, behind the two good candidates. The other lubricants appear to allow worse tarnish formation after

36 hours than the unlubricated control. Several other changes in the ordering at 24 and 36 hours suggest that CRB+R has not decreased in effectiveness at 36 hours as much as some of the other candidates, and that P4P3E has become worse.

These results suggest that the 81309 and NY 518 are effective tarnish preventatives at both time intervals. For shorter exposure, a number of the candidates afforded a modest amount of protection, but with longer exposure to sulfide, they became worse than the unlubricated control.

Studies were made on AR, CS, and SC connectors previously tarnished in $(NH_4)_2S$ in earlier studies. These were designed to simulate a connector that had been tarnished and exposed to the chemical refurbishing treatments, as well as to check for possible bias in the original rankings due to connector conditions. The tarnished connector sections were cleaned, detarnished, and chromated. Record was made of the previously applied lubricant. The current lubricants appearing to be best (e.g., NY 518, 81309) were applied to specimens previously tarnished with poorer lubricants (e.g., P4P3E) and vice versa. The previous-current lubricant pairs were the same for the CS, SC and AR connectors. The current and previous lubricants and the ranking based on the current lubricants is evaluated in Table 5. These "crossed lubricant" data show the same trend as the others, namely that 81309 and NY 518 are superior, and NY 515 is third.

Table 6 combines all data for the eight lubricants most frequently studied. The lubricants are listed in order of decreasing corrosion-prevention effectiveness. The significant distributions recapitulate the earlier trends. 81309 and NY 518, the top two candidates, and NY 515 as third-ranked fluid, are the only ones significantly better than unlubricated samples.

As a demonstration of the effectiveness of the candidate materials, their ability to prevent sulfide formation on pure silver was also examined. Coupons ~ 3 cm x 1 cm, cut from sheet stock of 99.9% Ag, were washed in ethanol and detarnished with the detarnishing procedure used for connectors. The central region of each coupon was coated with a test fluid in a film comparable to those studied on connectors. The Ag coupons were subjected to $(NH_4)_2S$ for 12 hours. Two unlubricated chromated NCOT sections were also present in the test chamber. The results are shown in the photograph of Fig. 4. The three fluids consistently ranking the highest in tests with connector sections, 81309, NY 518 and NY 515, are the only fluids that prevented tarnishing of the Ag. The other fluids tested had some preventive effect as compared to the unlubricated coupon at far right, but discoloration did occur on those specimens.

A similar test not pictured was made with lubricant-treated Ag coupons exposed to H_2S. The same three fluids allowed the Ag to remain untarnished. The mode of tarnish formation appeared different in the two test environments, with H_2S forming deeper pits and spots of very black tarnish vs. the more uniform discoloration obtained with $(NH_4)_2S$. On connectors, the test environments of $(HN_4)_2S$ or H_2S also appeared to produce different types of tarnish, but this did not appear to alter the ranking of lubricants.

III. Studies of Corrosion in Humid H_2S Atmospheres

A. Experimental Methods

Tests were made with intact, used connectors and NCOT connectors. Pins removed from both used and NCOT connectors as well as individual replacement pins from stock supply were studied using various combinations of the treatments, as shown in Table 2. H_2S tests were made at both 60°C and ambient temperatures for 12-hour intervals. The air-filled chamber was dosed with gaseous H_2S to an estimated 1000 ppm. Humidity was generated from a saturated oxalic acid solution (78% r.h. at 25°C) in a glass dish in the test chamber. Test chambers were arranged as in Fig. 2. Some individual pins or connectors were exposed to heat only or to water only for various periods of time. Corrosion-preventive fluids and methods of preparation and application were those described in Section I.

B. Results

A set of used WD connectors is shown in the photograph of Fig. 5. The lubricants 81309 (2A) and NY 518 (5A) were better corrosion preventives than the other organic fluids. The connector at the bottom of Fig. 5 is an AR NCOT connector that had been chromated by the manufacturer. This AR NCOT connector was affected less by H_2S than any of the unchromated lubricated WD used connectors.

The effect of H_2S on individual lubricated pins was similar to the connectors. Unlubricated pins that were WDC after being removed from used connectors fared better than removed pins that were not chromated, and also were better than replacement pins. On W or WD used pins, lubricants had a deleterious effect under these test conditions.

IV. Tests on Wired Connectors

A. Experimental

A new female NCOT connector was used as-received. Two connectors removed from service were washed and detarnished. The three female connectors and three male connector plugs with PCB fingers were wired at odd-numbered and lettered pins. The even-numbered pins served as spacers and unwired unlubricated controls.

Lubricants NY 515, NY 517, NY 518, 81309, and 81846 were applied to adjacent pairs of pins (e.g., 1 and A) and tested in a circuit with 2.5 V DC across 1100 Ω with 2 mA current. The lubricated NCOT connector and one detarnished connector were placed in the test chamber at 60° and 80% r.h. and dosed with H_2S to ~1000 ppm at 0 and 12 hours. One detarnished connector was maintained at ambient conditions. Individual wire connectors were used on each lead.

B. Results

After 12 hours, the NCOT connector was unchanged in appearance. Tarnish had begun to form on several pins of the WD connector exposed to H_2S. The WD connector at ambient conditions was also unchanged. After one week, without deliberate removal of H_2S, tarnish had formed on a number of pins of both the WD and NCOT connectors in the test chamber. The tarnish locations were random with respect to lubricated-wired or unlubricated-unwired pins. No visible tarnish appeared on the male PCB pins. After six months, all pins had tarnished essentially uniformly. The WD connector in the test chamber was worst, followed by the NCOT in the test chamber. The WD connector at ambient conditions tarnished to a much lesser extent. Male connector fingers showed beginnings of tarnish.

The main observation made was that no selective effect of electrification was seen with any of the specimens. H_2S was added to the test chamber only twice, at 0 and 12 hours. The test chamber atmosphere may have contained other sulfur-bearing contaminants (e.g., SO_2). Additionally, since it is not known with certainty that the tarnish is entirely sulfide, outgassing products and vapors from the rubber and phenolic components (24) present in the closed test chamber may have contributed to the overall corrosion. The corrosion film on the connectors exposed to H_2S was grey-brown, thin, and uniform, varying only in degree.

The WD wired connector pair at ambient (~25°C and 25% r.h.) had lubricated pins that were not corroded after six months, and the amount of tarnish formation (mostly on the unlubricated spacer pins) was not only considerably less than those exposed to H_2S, but it was multicolored rather than grey-brown.

A used WD unlubricated unwired female connector was exposed to only 60°C heated air by being placed in the oven outside of the closed dessicator H_2S test chamber. After three months, it had also formed a smooth, multicolored tarnish film that was more severe than that on the ambient air-exposed wired lubricated connector, and both of these were less severe than the wired pairs initially exposed to H_2S.

V. Discussion

In the evaluation of candidate fluids for corrosion protection, the 81309 spray consistently performed better than the other available fluids. NY 518 also has been quite good and is second only to 81309. NY 515 was rated third from the sulfide tests, whereas it was judged better than NY 518 in preliminary heating tests designed to assess stability to oxidation (9). The Au/Ag/Cu connectors and pure silver were used in sulfide tests, while 52100 steel was used in the oxidation experiment. NY 518 was found to take on a milky appearance after heating in air (9). This has been seen in other mixtures of polyphenyl ethers with hydrocarbons (25), but should not affect the sulfide corrosion-preventive behavior so long as a coherent film of the fluid is maintained. The lack of changes in appearance of NY 518 with time in sulfide tests and the substantial prevention of tarnish by very thin films of this material is testimonial to its effectiveness under these conditions.

A number of other candidates afforded an intermediate level of protection. While the polyphenylether-based NyeTack 518 is superior, a polyphenylether (4P3E) alone does not appear to be protective. This may be due to the tendency of polyphenylether fluids to not wet, i.e., to form a non-coherent film on a substrate, as surfaces were uncorroded where a film of 4P3E was coherent. Mixtures of 4P3E containing hydrocarbons, similar to NyeTack 518, do form coherent films (25).

NCOT sections scratched after chromating (CS) fared better than those which had been scratched prior to the chromating process (SC). Tarnish formed more intensely in the scratched regions of SC connectors and extended outward from the scratch site, and the scratched regions were more affected by the $(NH_4)_2S$ than other regions of the pins. In contrast, scratched regions of CS samples were not always darkened, but when corrosion did occur, it was dark in color and confined to the actual scratch area. Figures 6 and 7 are photographs of identically tested CS and SC sections illustrating this point, which may bear further investigation to elucidate this difference that occurred with all lubricants studied.

The discoloration from $(NH_4)_2S$ on connectors and pins differed visually from that obtained with H_2S in a humid atmosphere. These both differed from discolorations obtained from immersion in H_2O or from heating in air, although the H_2S and heated air samples were the most alike of those mentioned. Discoloration films produced in $(NH_4)_2S$ atmospheres were "rougher" and duller in appearance than the smooth, shiny, multicolored discolorations seen with H_2S or in heated air.

The NCOT sections exposed to $(NH_4)_2S$ were always corroded more severely on the back (solder lug) regions than the curved tops of the spring pins. Fronts and backs were thus ranked separately. During the sulfide exposure tests, connector sections were always standing on one cut end, as seen in Fig. 2. No difference was noted from end-to-end. Changing the test configurations to lying in various directions, front up, front down, or lying on phenolic side, did not alter this finding. Fronts and backs of connectors exposed to H_2S, however, were tarnished to an equivalent extent.

More extensive ranking evaluation was carried out with data obtained in $(NH_4)_2S$ environments than with H_2S environments. In each environment, as seen in Fig. 5 and in the data of Tables 3-6, the best fluid candidates for corrosion protection were 81309 and NY 518, followed by NY 515. Some of the candidate fluids with intermediate rankings were of different effectiveness in the two environments. In particular, the two fluorinated compounds looked promising in tests with H_2S, but fared poorly in $(NH_4)_2S$ tests.

Silver coupons exposed to humid H_2S at 25°C had an overall level of tarnish that was lower than that obtained with $(NH_4)_2S$, but formed small spots of deep black tarnish that were not seen on the coupons exposed to $(NH_4)_2S$, as shown in Fig. 4.

All of these contrasts suggest a difference in the corrosive behavior of $(NH_4)_2S$ and H_2S that may require further evaluation. Ammonia is a corrosive atmospheric component (14) and although not expected to form from $(NH_4)_2S$, its possible presence in sulfide tests should be investigated.

Pins that were removed from connectors always tarnished more quickly than the exposed regions of those intact in the phenolic connectors. The phenolic case of the connector was considered as a potential reason for this difference. Pins exposed to $(NH_4)_2S$ near a piece of the phenolic or loosely placed into a section of the case front tarnished as quickly as those isolated from the phenolic, showing that the mere proximity of phenolic was not the source of the difference.

VI. Conclusions and Recommendations

$(NH_4)_2S$ and H_2S sulfide tests showed two superior fluids, MIL-C-81309 and NyeTack 518, for corrosion protection of female connectors in the MARDAN system. This was the conclusion from studies made with pins alone, with used intact MARDAN connectors, and with segments of new connectors prepared to the old Au/Ag/Cu technology.

Detarnished old or new pins that were not chromated were easily corroded. The application of 81309 to detarnished pins rendered them resistant to corrosion to about the same extent as a chromated pin with no lubricant. The combination of chromating with 81309 was consistently a superior combination for corrosion prevention. NyeTack 518 in combination with chromating was always the next highly ranked, and in many cases equalled 81309. NyeTack 515 is a third choice for sulfide corrosion protection of connectors. Statistical analysis of ranking data on NCOT sections exposed to $(NH_4)_2S$ showed these three lubricants to always be the top-ranked candidates. This is in agreement with the protection of detarnished silver by MIL-C-81309 and NyeTack 518 shown in Fig. 4.

The life trends of the top two candidates appear favorable. The 12-, 24- and 36-hour rankings did not change for these candidates and long exposure to ambient conditions did not alter their effectiveness. A wired connector with the best candidate fluids at ambient conditions for six months suggested that the protection afforded by these two fluids was still operative. Some of the other compounds evaluated showed deterioration in effectiveness with time. MIL-C-81309 has already been subjected to extensive testing by Autonetics (10); NyeTack 518 would clearly be a good candidate for similar evaluation.

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Table 1. Corrosion Preventive Fluids and Properties

Code	81309	NY 518
Mfgrs. Name	Corrosion Preventive Compound Type C (CPC), MIL-L-81309	NyeTack 518
Purpose	Water-displacing, corrosion-preventive	Electrical contact lubricant
Composition	Petroleum sulfonate, 20%	Polyphenyl ether and hydrocarbon wax, 2%
Solvent	Petroleum spirits, 80%	1,1,1-trichloroethane
Additives	Antioxidant	Antioxidant
Physical State	Aerosol	Solution
Applic. Method	Spray	Swab
Film Type	Fluid	Fluid
Flammable	Yes	No
Flash Point	-	550°F (5P4E)
Viscosity, at 38°C	-	
Status	Commercial	Commercial
Mil.Spec.	MIL-C-0081309C (AS)	n/a
Source	CARE Laboratories, Inc. P.O. Box F, Collegeville, Pa. 19246	Wm. F. Nye, Inc. P.O. Box G-927 New Bedford, MA 02742
Reference	(13)	(14)

(continued)

Table 1 (continued)

Code	NY 515	NY 517	CRBLU
Mfgrs. Name	NyeTack 515	NyeTack 517	Cramolin (Blue)
Purpose	Contact lubricant and tarnish preventive	Contact lubricant	Anticorrosive electrical contact lubricant
Composition	Ultrahigh viscosity hydrocarbon oil and special binder, 10%	Proprietary, 10%	Proprietary
Solvent	1,1,1-trichloroethane	Freon 113	Proprietary
Additives	Antioxidant	Antioxidant	Proprietary
Physical State	Solution	Solution	Fluid
Applic. Method	Swab	Swab	Swab
Film Type	Fluid	Fluid	Fluid
Flammable	No	No	No
Flash Point	560°F (Base Oil)	-	-
Viscosity, at 38°C	2605 cs (base oil)	-	-
Status	Commercial	Experimental	Commercial
Mil.Spec.	n/a	n/a	n/a
Source	Wm. F. Nye, Inc.	Wm. F. Nye, Inc.	CAIG Laboratories, Inc., P.O. Box 64, 1175-O Industrial Ave., Escondido, CA 92025
Reference	(14)	(14)	(15)

(continued)

Table 1 (continued)

Code	CRRED	CRB+R	81846
Mfgrs. Name	Cramolin (RED)	Cramolin Blue and Cramolin Red	NRL MB20B
Purpose	Electrical contact lubricant	See CRRED and CRBLU	Lubricant for precision bearings
Composition	Proprietary	-	Polyol and diol esters
Solvent	Proprietary	-	-
Additives	Proprietary	-	Antioxidant, antiwear
Physical State	Fluid	Fluid	Fluid
Applic. Method	Swab	Swab sequentially	Swab from Freon 113 solution
Film Type	Fluid	Fluid	Fluid
Flammable	_	-	Yes
Flash Point	-	-	221°C
Viscosity, at 38°C	-	-	14.4 cs
Status	Commercial	-	Commercial
Mil. Spec.	n/a	n/a	MIL-L-81846
Source	Caig Laboratories Inc., P.O. Box 64 1175-O Industrial Ave., Escondido, CA 92025	Caig Laboratories, Inc., P.O. Box 64, 1175-O Industrial Ave., Escondido, CA 92025	Wm. F. Nye, Inc.
Reference	(15)	(15)	(16)

(continued)

Table 1 (continued)

	P4P3E	NAHEX
Code	MCS 210	Sodium Hexametaphosphate
Mfgrs. Name	High temperature lubricant	Corrosion Inhibitor
Purpose		
	Polyphenyl ether, 4P3E	Sodium hexametaphosphate
Composition	-	-
Solvent	-	-
Additives	Fluid	Solid, dissolved in H_2O
Physical State	Swab	Swab
Applic. Method	Fluid, autophobic	Solid
Film Type	Yes	-
Flammable	Initial decomposition >840°F	
Flash Point		
	69.5 cs	
Viscosity, at 38°C	Commercial	Commercial
Status	n/a	-
Mil.Spec.	Monsanto Chemical Co. St. Louis, Mo.	Laboratory source
Source		
	(17)	(18)
Reference		

(continued)

Table 1 (continued)

Code	SG624	FC723	FL383
Mfgrs. Name	G624	NyeBar Type W	Bray 3L-38RP
Purpose	Water repellent and corrosion protection for electrical application	Oil resistant barrier film	Inert low vapor pressure lubricant
Composition	Silicone + gelling agent	Perfluorometha-crylate 0.2%	
Solvent	-	Freon 113 + Perfluoroether	
Additives	-	-	Antioxidant
Physical State	Gel	Solution	Bled oil of grease
Applic. Method	Swab	Swab	
Film Type	Tacky	Solid	
Flammable	-	No	
Flash Point	-	-	
Viscosity, at 38°C	-	-	
Status	Commercial	Commercial	Commercial
Mil.Spec.	MIL-S-8660B	MIL-	-
Source	General Electric Co., Silicone Products Division, Waterford, N.Y.	Wm. F. Nye New Bedford, MA.	Bray Oil Products, Inc.
Reference	(n/a)	(19,20)	(21)

Table 2. Sulfide Exposure Test Modes for Connectors and Pins

Test Conditions	Connectors	Treatment (with & without fluids)
I. $(NH_4)_2S$, ambient	NCOT	AR
		W + D + C
		W + D + S + C
		W + D + C + S
		W + D + S + C, W + D + C (crossed
		W + D + C + S, C + D + C experiments)
Pins		
	NCOT	AR
		W
		W + D
		W + D + C
	Replacement Ag/Cu	AR
II. H_2S, 60°C		
	NCOT	AR
	Used	W + D
Pins		
	NCOT	AR
	Replacement Au/Cu	AR
	Used	W + D
III. Air 60°C		
	Used	W + D
IV. Electrified Connectors		
H_2S, 60°C	NCOT	AR
H_2S, 60°C	Used	W + D
Ambient	Used	W + D

Code: W = Washed
D = Detarnished
C = Chromated
S = Scratched
AR = As-received, used as controls in all studies
NCOT = New Connector made to Old Technology (Au/Ag/Cu)

Table 3. Ranks and Distributions of Lubricants for Corrosion Protection of Female Connectors Using Combined CS and SC Data from $(NH_4)_2S$ Exposure.

	Combined						Backs			Fronts		
				Experimental Range								
Lubricant	Rank	Signif. Distrib.	Mean	Minimum Rank	Maximum Rank	N	Rank	Mean	Signif. Distr.	Rank	Mean	Signif. Dist.
81309	1	A	1.4	1	3	10	1	1.2	A	1	1.5	A
NY518	2	AB	2.3	1	4	10	2	2.2	A	2	2.3	A
NY515	3	B	3.7	2	6	10	3	4.0	AB	3	3.5	AB
CRBLU	4	C	5.5	4	8	10	5	6.0	BC	4	5.8	BC
CRB+B	5	C	5.7	4	9	10	4	5.8	BC	5.5	5.7	BC
NOLUB	6	C	6.0	1	10	10	7	6.5	BC	5.5	5.7	BC
81846	7	CD	6.6	3	10	10	6	6.0	BC	7	7.0	CD
NY517	8	CD	7.1	4	10	10	8	6.5	BC	8	7.5	CD
P4P3E	9	DE	7.85	3	10	10	9	8.2	C	9	7.6	CD
NAHEX	10	E	8.85	5	10	10	10	8.5	C	10	9.1	D

Means with same letter are not significantly different from each other at the $\alpha = 0.05$ level, using Duncan's t-test.

Table 4. Exposure Time Effectiveness of Ten Lubricants for Corrosion Protection on NCOT in $(NH_4)_2S$ Using Duncan's Test on Combined CS and SC Data.

	24-Hour Exposure Time			36-Hour Exposure Time		
Lubricant	Rank	Mean	Significant Distributions*	Rank	Mean	Significant Distributions*
81309	1	1.3	A	1	1.5	A
NY518	2	2.0	AB	2	2.8	AB
NY515	3	3.7	BC	4	3.8	AB
CRBLU	4	5.0	CD	6	6.2	CD
CRB+R	5	5.8	DE	5	5.5	BCD
81846	6	6.2	DE	7	7.2	D
NY517	7	6.7	DE	8	7.8	D
P4P3E	8	7.4	EF	10	8.5	D
NOLUB	9	7.7	EF	3	3.5	ABC
NAHEX	10	9.2	F	9	8.2	D

* Means with the same letter are not significantly different from each other at the $\alpha = 0.05$ level.

Table 5. Rank and Distribution of Crossed Lubricant Corrosion Prevention with 36-hr $(NH_4)_2S$ Exposure

Current Lubricant	Rank	Mean	Significant Distribution*	Previous Lubricant
81309	1	2.2	A	NAHEX or CRR+B
NY518	2	3.5	A	P4P3E or CRBLU
NY515	3	3.5	AB	CRRED
CRBLU	4	6.5	BC	NY515
NOLUB	5	7.8	CD	NY517 or 81309
81846	6	9.0	CD	NY518
NY517	7	9.5	CD	81846
NAHEX	8	10.5	D	NOLUB

Data for the 11 lubricant combinations were grouped by the 8 current lubricants.

*Means with the same letters are not significantly different at the $\alpha = 0.05$ level.

Table 6. Lubricant Effectiveness over all Test Conditions for NCOT Corrosion Protection from $(NH_4)_2S$ Using Duncan's t-Test†

Lubricant	Overall Rank	Significant Distribution*	Experimental Rank Range Mean	Min.	Max.	No. of Samples
81309	1	A	1.4	1	3	14
NY518	2	A	2.0	1	4	14
NY515	3	B	3.3	2	5	14
CRBLU	4	C	4.9	3	7	14
NOLUB	5	C	5.7	1	8	14
81846	6	C	5.7	3	8	14
NY517	7	C	5.8	3.5**	8	14
NAHEX	8	D	7.0	5	8	14

* Means with same letter are not significantly different from each other at the $\alpha = 0.05$ level.

** Tied rank 3 and 4.

† Total degrees of freedom = 108. Data from all AR, CS, SC, and replications.

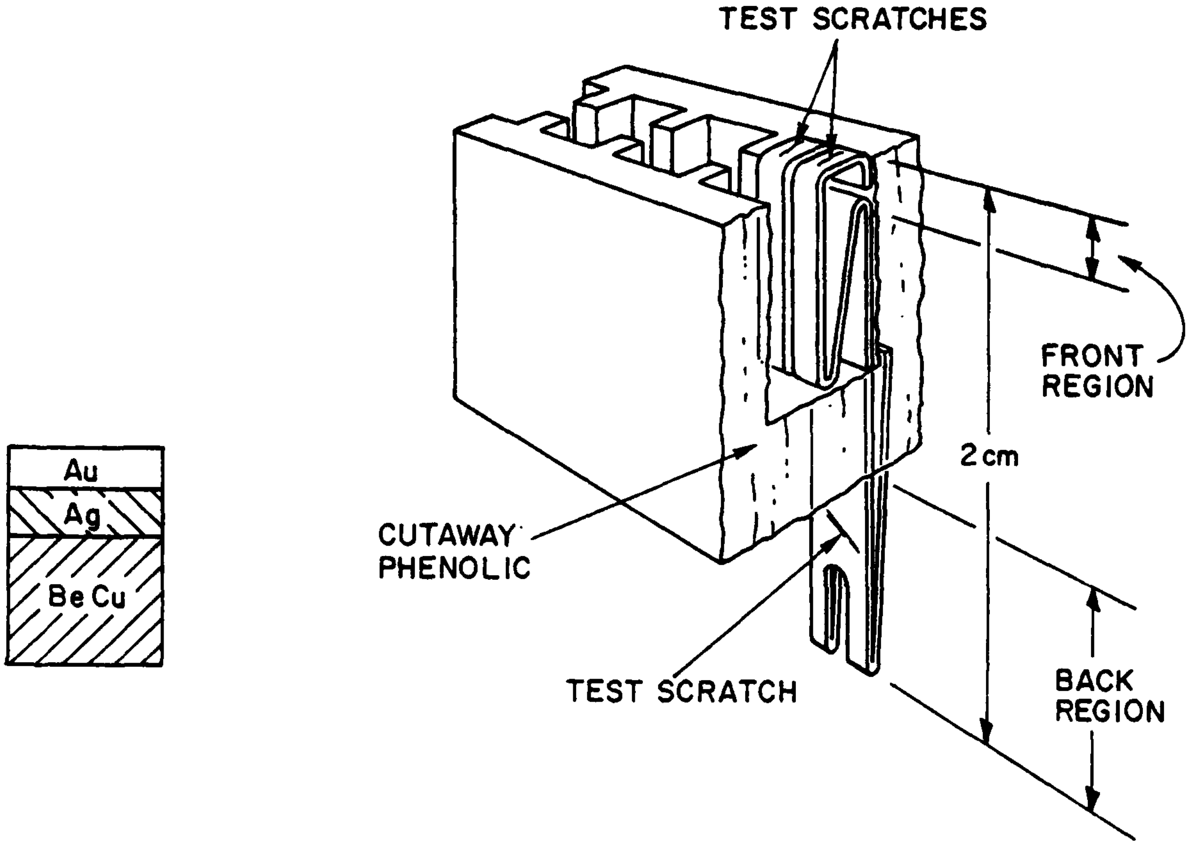

Fig. 1 — Sketch of Au/Ag/Cu composition of MARDAN connector spring pins, and pin conformation. Front and back regions in ranking tests and the locations of scratches are indicated.

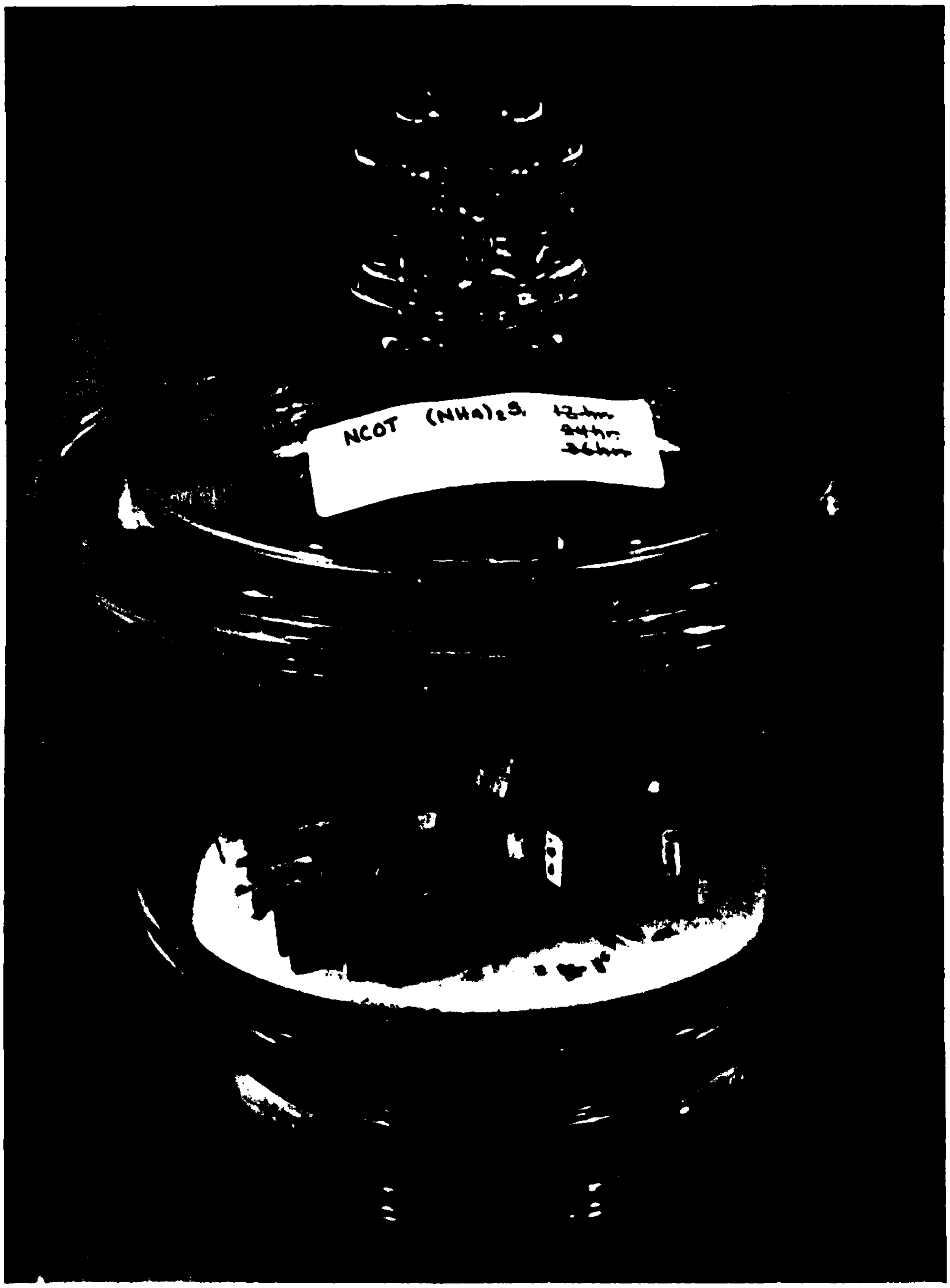

Fig. 2 — Test configuration for NCOT sections. The sulfide atmosphere was generated from a small dish of dilute aqueous $(NH_4)_2S$ below the specimens.

Fig. 3 — Typical ranking of back regions of NCOT sections after 36-hour sulfide exposure. The samples shown were detarnished and chromated, then scratched (CS). Corrosion on the front regions of these specimens corroded in the same order but to a lesser degree. Sections labeled 6 and 7 were inadvertently exchanged during photography.

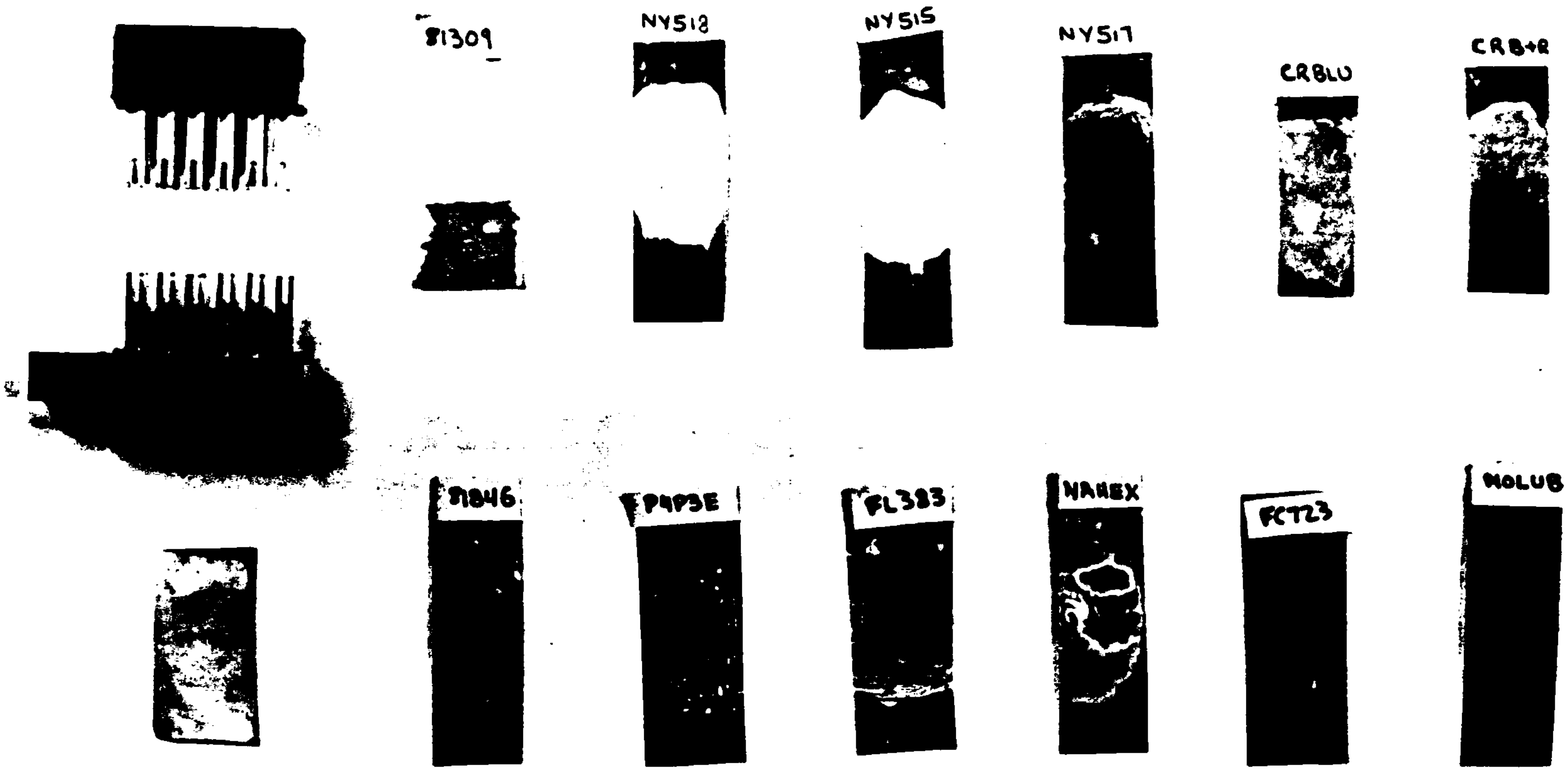

Fig. 4 — Silver coupons with protective lubricants after 12-hour exposure to $(NH_4)_2S$ showing the relative efficacy of the test fluids applied to the central region of each detarnished coupon. The unlabeled coupon at the left was unlubricated and exposed to room air for one week. The unlubricated, chromated connector sections at the left were exposed to $(NH_4)_2S$ with the coupons, and show only the light tarnish typical of 12-hour exposure.

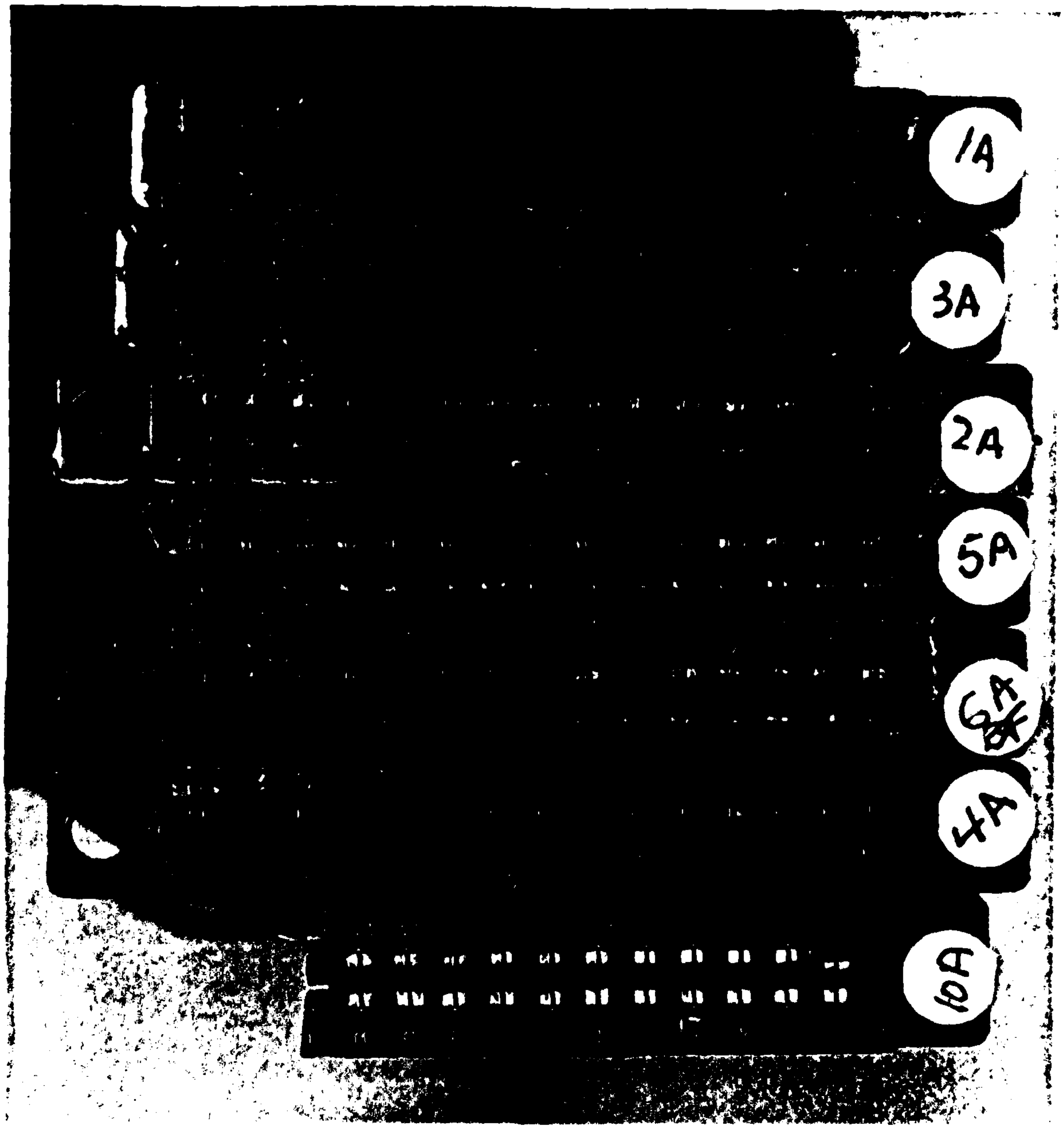

Fig. 5 — Detarnished used MARDAN female connectors with various lubricants after H_2S exposure at 80% r.h. and 60°C. Connector 1A was detarnished only with no lubricant, and is the most heavily corroded. The other used connectors were lubricated according to: 2A = 81309, 3A = NY 515, 4A = NY 517, 5A = NY 518, and 6A = FC 723. The connector labeled 10A was a NCOT connector with no lubricant.

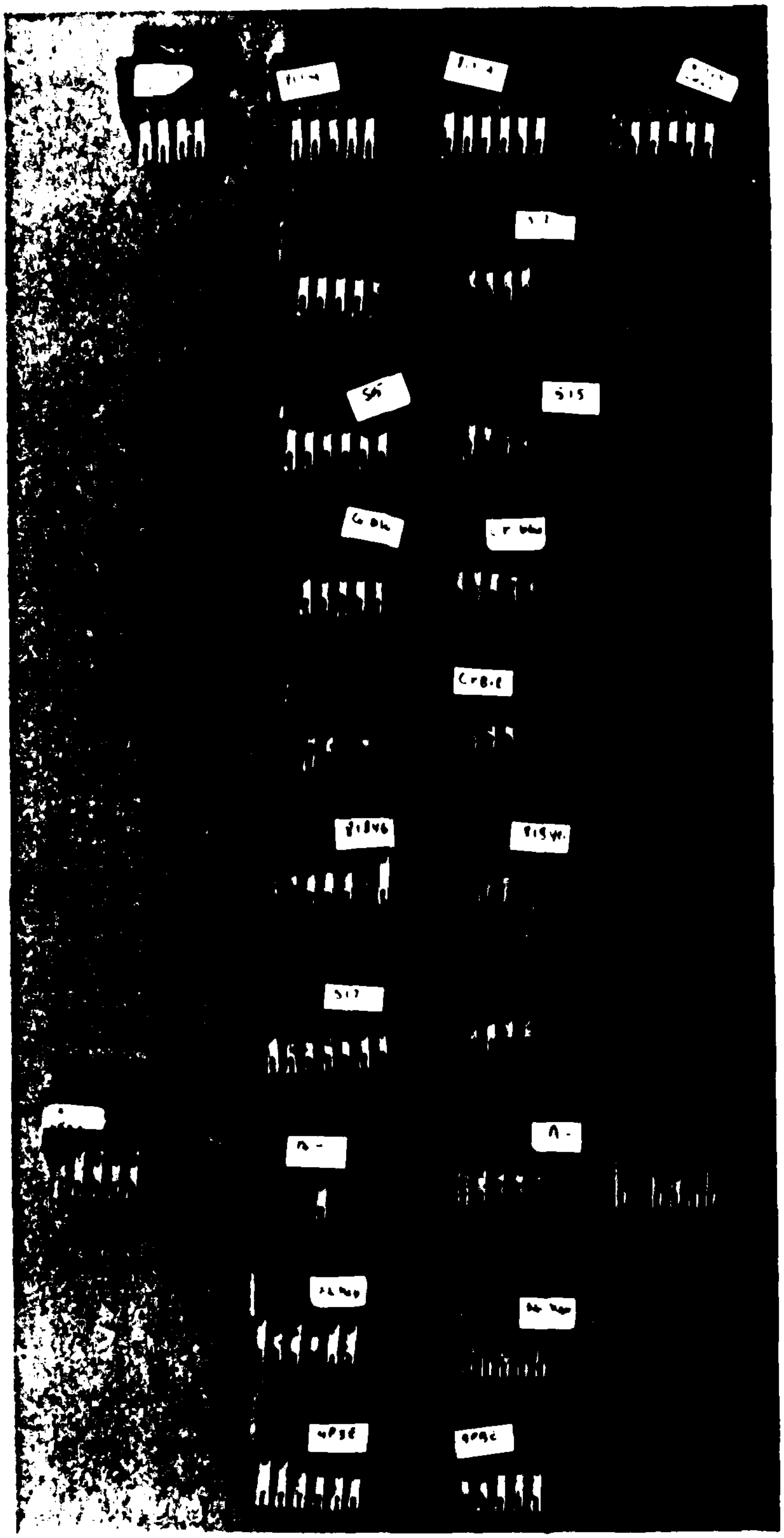

Fig. 6 — The back regions of chromated, then scratched (CS), and scratched, then chromated (SC) connectors after exposure to $(NH_4)_2S$. On the CS samples at left, the tarnish was confined to the scratches. In contrast, the tarnish on SC samples at right is seen to spread from the scratches. Scratches on the curved fronts of connector pins tarnished in the same way as those shown here.

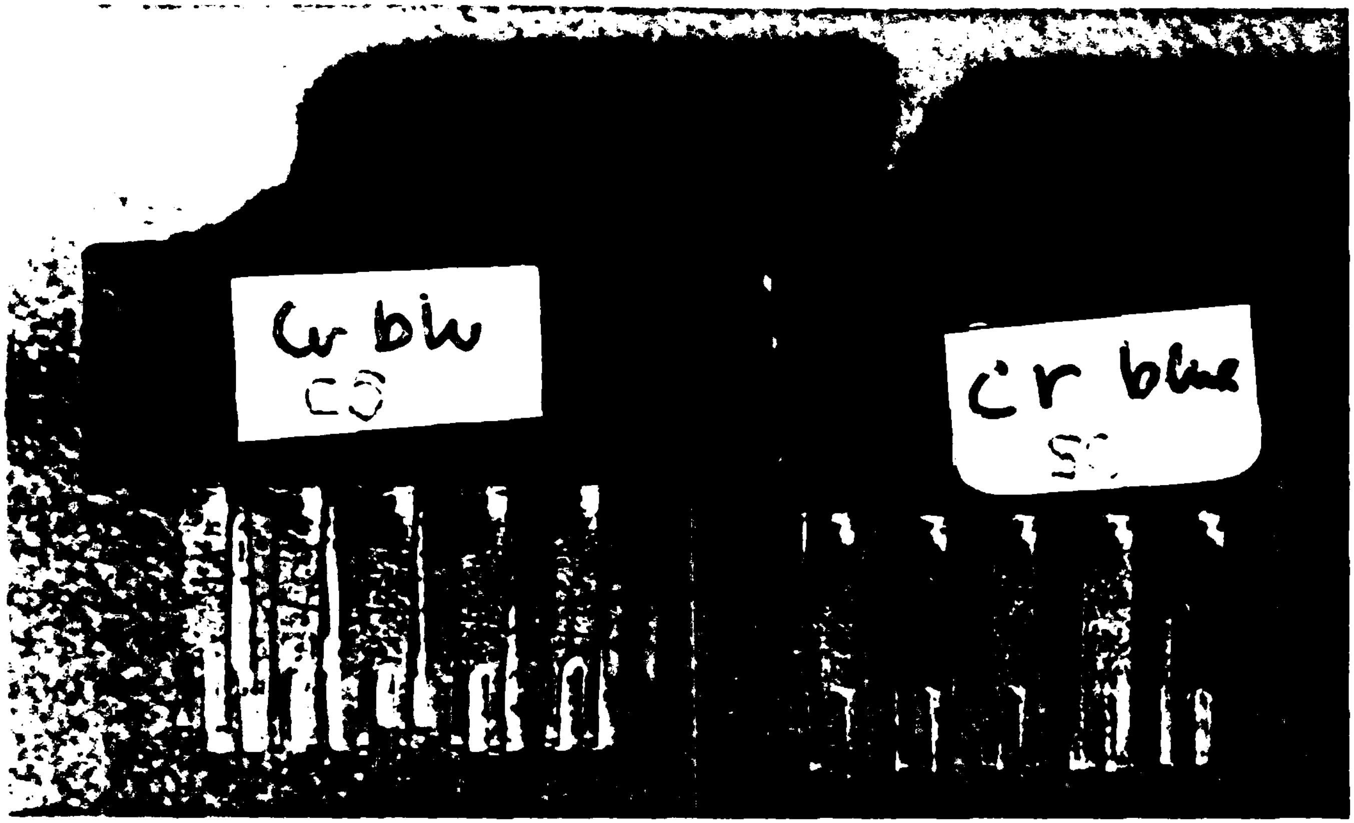

Fig. 7 — A close-up view of a CS and SC connector from Fig. 6, showing the difference in the tarnished scratched regions of the otherwise identical samples

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