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Proposal/Agreement No. 944-H-0702R

Mr. Alan J. Olson
B.F. Goodrich Chemical Division
Technical Center
Moore and Walker Roads
Avon Lake, Ohio 44012

Dear Mr. Olson:

REVISION OF PROPOSAL ON: CORROSIVITY OF SMOKE

This letter is a revised proposal (per our telephone and fax communications) from Battelle in response to my recent visit to your facilities. The subject of the proposal is "Corrosion of Metallic Materials by Smoke from Burning Plastics".

Although this proposal is being directed to you, it is our understanding that if this work is conducted, it would be funded by the Vinyl Institute. It is also our understanding that the studies at Battelle would probably be part of a larger program in which some studies would be conducted at B.F. Goodrich. Although we believe that any work resulting from this proposal would be under a contract between the Vinyl Institute and Battelle, there is some uncertainty on our part regarding how any formal agreement should be worded. Therefore, we have not submitted our standard research agreements with this proposal. If and when a decision is made to proceed with this program, we propose that the contractual matters should be resolved at that time.

It is our understanding that you will be discussing this proposal at a meeting on or about January 19, 1993. We are submitting this proposal well in advance of this meeting for your review. Therefore, if it is your opinion that changes should be made to the proposal in advance of this meeting please let us know.

BACKGROUND

In recent years there has been considerable interest in the subject of the effects of smoke/corrosive gases released from various materials such as plastics. Of particular interest are the effects of corrosive gases on electrical and electronic equipment. One of the reasons for this high level of interest is the recognition that the levels of critical pollutants which may affect the reliability of electrical equipment may be orders of magnitude less than the levels considered to be toxic towards humans. Although the concentrations of critical pollutants released during a fire may be measured in tens of parts per million, and are well above the levels of a few parts per billion which may effect modern electronic equipment, the net effects from a fire may be partially offset by the fact that high concentration releases are of relatively short duration in comparison to the long term, low concentration, effects normally associated with corrosion. These observations indicate that to some degree it is the integrated dosage of pollutants which will affect corrosion. Unfortunately, the exact relationship between high concentration, short term, effects and the reverse is not known.

Extensive studies at Battelle and elsewhere have shown that for the corrosion of electrical equipment, two types of pollutants are of particular importance. These may be termed reactive chlorides and reactive sulfides. These findings are particularly significant, since it is well known that high concentrations of reactive chlorides are often associated with gas releases from burning plastics. It is also known that other important pollutants including other halogenated species, oxides of nitrogen, and/or ammonia when present at relatively high concentrations may also affect corrosion of electronic equipment.

In reality, the problem of electronics corrosion by air pollutants is far more complex than that which might be inferred from a study of the effects of single gases. It is clear that corrosion is usually the result of a complex, synergistic, interaction among multiply pollutants, humidity, and temperature. This fact is particularly significant to the present topic, since it is our opinion that any attempt to measure environments in detail and to relate a multitude of variables to corrosion is likely to be unsuccessful. Instead direct measurements of corrosion on **relevant materials** has been shown to be the most effective means of evaluation long term corrosive effects.

Recently, technical publications have appeared in the literature in which attempts have been made to evaluate smoke corrosivity. It appears that in most of these studies attempts have been made to use standardized procedures for smoke generation but which were not specifically developed for allowing controlled corrosion studies. In effect, it appears that most of the recent studies simply used "add on" test chambers into which combustion products were allowed to flow. Unfortunately, it appears that the critical variables which can effect materials corrosion were not closely controlled. As a result, some of the data appear to be non-reproducible and/or contrary to expectations.

As a result of the uncertainties surrounding existing data and test methods, the Vinyl Institute is considering a research program in this subject area. The scope of the research would involve the corrosion of selected metals and the reproducibility of corrosion produced by the products from the burning of selected plastic materials.

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PROPOSED RESEARCH PROGRAM

The final objective of the research program which is being proposed will be to demonstrate that a technique known as the NBS Cone Burner does produce corrosion of metallic systems. Emphasis is being placed on the NBS cone method at the request of the Vinyl Institute, since this method appears to be in particular favor for other studies related to the burning of plastics.

While the preceding would be viewed as the overall objective of this program, discussions between Battelle and B.F. Goodrich have suggested that the experimental program should be conducted in phases. The remaining portion of this proposal will, therefore, outline the experimental program which was the result of these discussions.

PHASE 1

Experimental Approach

An objective in the early stage of this program would be to develop a test system and procedures which would produce corrosion from the products of burning plastics and would do so in a reproducible manner. This means that the test system should provide both the means for combustion product generation, the means for metering products into a corrosion chamber, and a corrosion chamber which will provide the means for control and monitoring of all of the critical variables. With respect to the latter item, a desirable objective would include a test system which is as simple in design and operation as possible. We can note at this point that as a result of ongoing studies in the subject of the corrosion of electronics, Battelle has gained considerable experience in the design and monitoring of similar test chambers.

The first phase of the program is designed to establish that these requirements can be met using the NBS cone burner. For the purposes of this phase of the project, the Vinyl Institute will provide (or reimburse Battelle) for a suitable NBS cone burner system, for use in Battelle's lab.

The atmosphere above the cone burner will serve as the source of relevant pollutants. The cone burner with samples of plastics will be operated under standard conditions for the NBS cone calorimeter test. This gas stream would act to both support the combustion process and serve as a carrier gas stream to sweep pollutants into the corrosion chamber. If necessary, a static mixer or multi-port tube will be used to ensure that the effluent stream from the burner represents an isokinetic sample to the corrosion chamber.

The corrosion chamber that is proposed for this work would be of the same design as presently in use at Battelle for studies of the corrosion of electronic components by operating environments. In fact, Battelle already has available a number of chambers in varying sizes and one of these would be dedicated to this study. The materials of construction of the test chamber would be Plexiglas®. The chamber would have a capability to be heated and would typically operate at a temperature of about 30 C. However, condensation may occur within the test volume. If it is determined that this condition will occur, predilution of the pollutant stream with dry air will be explored.

The chamber would operate as a continuous gas flow system. This is considered essential based on past experience in order to control the corrosion process. In addition, the chamber would be provided with a means of air circulation in order to assure that uniform conditions can be maintained throughout the chamber. Presently, small muffin fans are used for this optional purpose. Finally, the basic chamber would be provided with means for humidity control.

The features just discussed should serve to outline the main features of the corrosion test exposure system. The following portions of this proposal will describe some of the initial experiments which are considered important to establish operating conditions. Also described will be additional details concerning samples, and monitoring of the corrosion processes.

Test Samples - Plastics

Initial discussions with B.F. Goodrich have suggested that three polymers should be used for these studies. These include (1) PVC, (2) polyethylene (neat), and (3) nylon.

It is understood that B.F. Goodrich could provide the polymers to be used in this work. The exact form/morphology of the polymers remains to be defined.

Test Samples - Corrosion Monitors

Battelle has conducted extensive monitoring of field operating sites for electronics worldwide. One objective of this work has been to develop monitoring techniques which will provide data on a short term basis which are directly relevant to long term reliability problems due to environmental corrosion. For reasons outlined earlier, the Battelle studies have emphasized direct, integrated monitoring of corrosion using various materials and sensor methods these techniques are well developed and are proposed for use in this study.

Three types of monitoring methods are proposed. These may be described as (1) passive sensors/coupons, (2) active sensors for continuous corrosion monitoring, and (3) fine line, intradigitated patterns for detection of electromigration.

The passive sensor method is particularly applicable, since it can provide a wealth of information on both corrosion rates and corrosion products. It is also a relatively low cost method which has been applied extensively in the development of field data bases.

At least four materials are proposed for use as passive sensors. These are copper, silver, nickel, and "porous" gold (thin gold plating over nickel over copper). Battelle could provide a detailed justification for the use of each of these materials if necessary. However, we may summarize by indicating that each of these materials offers unique advantages in their ability to respond to critical pollutants in the environment.

It is planned that at a first level of analysis, the copper, silver, and nickel samples will be evaluated by weight change. It is recognized that this analysis may be complicated by contributions from both particulates/smoke and corrosion. However, attempts will be made to separate these two contributions. If this work is successful, it could provide potentially important information regarding particulate deposition rates in addition to corrosion.

Once the weight change analysis has been completed, the silver and copper samples can be analyzed by a very useful technique which will examine only the corrosion films. This technique is known as cathodic reduction. It is a destructive, electrochemical method of analysis which will provide the information on both the amount of corrosion as well as the corrosion products. It is this technique which has been used extensively for the analysis of surface films produced in field environments.

Finally, the porous gold sensors are particularly interesting for two reasons. First, they can serve as permanent, visual indicators of corrosion. Such samples have proved to be very effective in demonstrating relative severity (or lack of severity) of environmental corrosion on a material system, which is very relevant to electronics. It should also be noted that at a technical level this material system is actually a very sensitive indicator of the presence of reactive chlorides in an environment.

The preceding discussion of the passive sensor method has described a procedure which at a minimum could be sufficient for the purposes of this program. However, the two other monitoring methods which are relatively easy to implement at Battelle can provide important information on a continuous basis. The first is an active sensor method. This type of sensor operates on the basis of detecting small resistance changes on an active element. These elements can be made of different materials, but for use in this program, copper sensors are recommended. Such a system has been developed at Battelle which operates under computer control. It is proposed that such a system will be used in all experiments in this program for the continuous monitoring of the corrosion process.

The final monitoring method, which will also be continuous, will examine a particularly relevant failure mechanism in field environments. This is shorting/electromigration between closely spaced conductors having an electrical bias between them. It is recognized that in the processes being examined, shorting could be produced by any or all of the following effects. These are (1) ionic contaminants in particulates, (2) conducting particulates such as carbon, and/or (3) corrosion products. While it may be difficult to separate these effects into fundamental causes, the measurements may still prove to be valuable as a means of describing the severity of corrosion. The techniques and samples for this type of work are already available at Battelle.

Test Procedures

It is expected that a significant portion of the work conducted in Phase 1 will involve the development of the detailed test procedures. As indicated earlier, it is expected that this work will be done in cooperation with and guidance received from B.F. Goodrich. Their important inputs will involve the operation of the furnace and the combustion process. Based on past Battelle experience, it is believed that the developed of an optimum procedure will involve the following issues.

(1) The duration of the combustion process.

(2) The fraction of the combustion products to be metered into the test chamber or, as an alternative, the relationship between the flow from the combustion stream/carrier gas and fresh make up air.

(3) Overall operation to maintain constant temperature and humidity conditions and to avoid condensation.

It is expected that initial experiments to resolve these issues would be conducted with one standard material. It is proposed that this material would be polyethylene, in order to establish a baseline.

Once the test conditions have been optimized, then a series of runs would be conducted under "standard" conditions. These tests would be made to meet the program objectives including examination of test reproducibility. For this purpose, it is planned that a minimum of three independent runs would be made for each material.

At the present time, the format of a test run has been generally defined. This is, of course, subject to change as the initial data are developed. The combustion and exposure conditions will be established through a process of optimization in order to allow corrosion to proceed at a reasonable rate from a measurement standpoint. Once combustion was complete, conditions would be maintained for a period of several days or to a point at which corrosion, as determined by continuous monitoring, had essentially stopped or had decreased by at least one order of magnitude. At this point, and as a final step, the relative humidity would be increased to about 70 percent RH. Beyond this point, corrosion and/or electromigration would be monitored over a period of several days, if necessary, to fully define the effect of hygroscopic corrosion products on either or both of these processes.

Once the test as just described was deemed to be complete, the corrosion test coupons would be retrieved for analysis as described earlier. The two types of active monitors as discussed earlier will essentially be in the form of printed circuit cards with active metallic elements. They will also have deposited on their surfaces particulate matter and/or ionic contaminants. It may prove to be desirable in a later phase of the program for a more detailed characterization of these materials to be made. Therefore, these samples when they are removed from the test chamber will be carefully preserved and packaged to retain the materials on the surfaces and to avoid any extraneous contamination.

PHASE 2

Phase 2 is viewed as an optional extension of the studies proposed in Phase 1. The objective of the Phase 2 work would be to conduct selected and detailed analysis of the gaseous species and/or the ionic contaminants deposited on surfaces.

The results to be obtained in Phase 1 cannot be predicted at this time. The results obtained from the corrosion monitors may present a totally adequate picture of corrosion and give a good indication of the active species which produced corrosion. The reverse is also true. In addition, and as a result of discussions with project monitors at the time, it may be considered desirable to conduct more detailed analysis.

If analysis are to be made, two techniques will be considered. First, for analysis of the gas streams, gas chromatography coupled with mass spectrography will be used. In addition, or as an adjunct to these analysis, it may be desirable to collect samples in an aqueous media for a determination of ionic species. The latter analysis may, in fact, be much more relevant to the overall corrosion processes.

As discussed earlier under the Phase 1 studies, the particulates deposited on surfaces are of particular interest. It is well established that the residual ionic content on circuit cards or other electronic surfaces is directly related to failure rates. Therefore, it is proposed that another level of analysis to be considered will be a determination of the type and concentration of ionic species resulting from the combustion process. These analysis will be made by ion chromatography and will use the circuit card surfaces of the active sensors as described in Phase 1.

PHASE 3

The objective of the Phase 3 studies will be to apply the technology and experience gained from Phases 1 and/or 2 for use with the NBS Cone Method. It is expected in this portion of the work that most of the actual experimental work would be conducted at B.F. Goodrich. The reason for this is that a cone burner is in place at B.F. Goodrich, and there is considerable experience in operating this unit. Furthermore, it would be impractical for Battelle to duplicate this facility.

Details of a Phase 3 study remain to be resolved. However, in principal, the nature of the work would be as follows. First a test chamber would be constructed to duplicate the one used in the Phase 1 studies. This assumes that the chamber would permanently reside at B.F. Goodrich. An alternative which may be possible would be for Battelle to loan the test chamber to B.F. Goodrich.

For whatever approach is used, it is expected that Battelle project personnel would periodically visit B.F. Goodrich to interface the test chamber and supporting facilities to the cone burner. Beyond this, Battelle personnel could provide whatever level of support would be requested as mutually agreed upon at that time.

REPORTING

During the course of this study, it is expected that close communication would be maintained between Battelle project personnel and whoever is designated by the Vinyl Institute as the cognizant project monitor. If the project monitor is other than personnel at B.F. Goodrich, it is also expected that a close working relationship would be maintained with the latter.

Battelle is proposing that a brief monthly status report would be issued during the course of this program. In addition, a final summary report would be issued at the completion of the Phase 1 studies. An alternative reporting schedule could, of course, be established by mutually agreement.

TIME AND COSTS

We estimate that the studies described under Phase 1 of this proposal could be initiated within a period of several weeks following the establishment of a research agreement and authorization to proceed with Phase 1 of this work. Thereafter, we are estimating that a period of 2 months would be required to complete the initial equipment setup in preparation for the first test runs. An additional 3 months should be required to establish the optimum test conditions. Once these are established, we further estimate that about 4 months should be required to complete the actual test runs on the three materials, which we are proposing would be conducted in triplicate.

In order for us to complete all of the proposed work under Phase 1, including the actual experimental work, data analysis, and reporting, we are proposing that a contract period of 12 months should be established.

The estimated cost for the Phase 1 studies as proposed is $66,000. This cost is based on the assumption that there will be no extraordinary expenses at Battelle associated with the installation of the NBS Cone Burner. If this is not the case, then Battelle would reserve the option of renegotiating the estimated costs.

At this time, we are submitting a formal proposal only for the Phase 1 studies. This includes time and cost estimates. The Phase 2 and 3 studies, if conducted, should be the subject of a discussion and negotiations in the future. However, for preliminary estimation purposes and based on our understanding of the work which might be conducted by Battelle, we would estimate that the costs for each phase could be in the range of $25,000 to $30,000 each.

CONTRACTUAL DETAILS

As indicated earlier, Battelle is not submitting actual research agreements at this time. We would be glad to do so following further discussions and/or possible modifications to the Phase 1 proposal.

Any questions relating to technical matters regarding this proposal should be directed to Mr. W. H. Abbott at 614-424-4198. Mr. Abbott will serve as the program manager for this work and will play a major role in the conduct of the studies.

Any questions relating to contractual matters and/or payments should be directed to Ms. Christina L. Rotunda at 614-424-5192.

We look forward to hearing from you and to the possibility of conducting this interesting and very significant study for the Vinyl Institute.

This offer shall remain valid for a period of sixty days from the date of this letter.

Yours truly,

W. H. Abbott
Projects Manager
Corrosion and Electrochemistry
Technology Group
Metals and Ceramics Department

WHA:csk

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