

PHYSICAL DAMAGE FORMATION ON AUTOMOTIVE FINISHES DUE TO ACIDIC REAGENT EXPOSURE

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ABSTRACT

Several types of automotive finishes with clear coatings were exposed to drops of acidic reagents at 54 C. Surface damage was examined using visual observations, reflection optical microscopy, SEM, EDS, and profilometry. Reflection microscopy was the most useful technique for observing surface damage. Scanning electron microscopy provided sulfur mappings through the use of an EDS attachment.

A chamber dew with pH level of 3.4 created in a smog chamber designed to simulate real environmental conditions was highly detrimental to the finishes with damage concentrated in a ring with a diameter less than the original drop size. The form of this damage suggests a free energy minimization process favoring a concentration of the damaging reagent at the edge of the evaporating drop where stable nuclei are thought to form. Continued heating of the samples after the drop evaporation resulted in damage that increased with time, with most of the visual damage located underneath material deposited from the evaporated drop.

INTRODUCTION

Environmental damage to automobile paints has been observed recently. This damage is generally in the form of circular, elliptical, or irregular spots that cannot be removed by washing¹. The major automotive manufacturers in the U. S. and other countries have some concern regarding the effects of acidic pollutants on automotive paints². It is suggested that newer automotive paint formulations which contain unpigmented surface clear coats are highly susceptible to acidic pollutant caused damage².

Our studies have attempted to reproduce this type of damage through exposing several types of automotive paints to a variety of acidic reagents with the objective of obtaining a

better understanding of the paint degradation process. We also were interested in evaluating techniques to assess the paint's surface damage. Such information would be helpful in formulating paints that are more resistive to acid precipitation.

J. White and W. Rothschild linked acidic deposition/acidic pollutants to automotive paint damage³. They observed spotting and in some cases pitting in locations on automobile paint surfaces when vehicles were exposed in the field in Israel. They were able to reproduce the color changes of the field exposed paints by spotting the specimens with either nitric or sulfuric acid.

The natural environment is very complex and it is difficult to isolate the effects of acidic pollutants from other variables for field exposed paints. It is also difficult to determine which techniques and parameters are optimum for determining the damage levels of paints after exposure. Here we extend the spotting type tests done by White and Rothschild and others by using acidic reagents that closely resemble environmentally produced precipitation. In an environmental research chamber at North Carolina State University, it is possible to prepare complex mixtures of acid dew of varying composition, which are representative of dews formed in real atmospheres. The composition of these dews can be easily controlled making them useful for the damage analysis of paints. Several types of automotive paints with clear coatings were exposed to these chamber dews and a variety of other acidic solutions. In the study reported here, emphasis was on characterizing the physical surface damage and proposing a possible model for the damage process.

EXPERIMENTAL METHODS

Paint Samples Studied

Several types of paint samples on sheet metal substrates were supplied by an automotive paint manufacturer. All samples were 10 cm by 15 cm with a total thickness (substrate plus paint) of about 0.84 mm. The paints were the same except for differing clear coat compositions. Based on information provided by the company, the most likely compositions were determined. All the paints had a black pigmented base coat which consisted of an hydroxyl-containing acrylic resin crosslinked with melamine formaldehyde.

Exposure Procedures

The paint samples were first washed with deionized water and then buffed lightly with a chamois before heating in order to remove dust from the surfaces of the sample. Then three 30 μ L drops of a pH 3.4 chamber dew produced in a smog chamber designed to reproduce real environmental conditions were pipetted onto the surface of the plate equal distances apart. Unless otherwise indicated, the plates were then placed into an oven and heated at 54 C for 50 minutes. After exposure, the plates were removed from the oven, allowed to cool, and then rinsed with deionized water and hand buffed immediately to remove surface deposits.

RESULTS AND DISCUSSION

The exposure method used in this study simulates the outdoor damage process of

automobile paints due to exposure to precipitation followed by heating from the sun. Temperatures during outdoor exposure can commonly exceed 90 C¹. In these experiments, exposures at 54 C for 50 minutes were used in order to observe damage levels under moderate exposure conditions. A spot type test was used to simulate the damage process that occurs after rain or dew exposure to automobile paints. Beading of water on the paint surface occurs during the drying process after rain or dew exposure which forms drops on the paint surface. The exposure of the paints to reagent drops in the spot test simulates this type of exposure and this type of test also permits comparisons with adjacent unexposed areas of the paint.

Reflectance Microscopy Observations

Ring shaped blistering damage was observed on all the paint surfaces. Figure 1 is of a paint surface with a clear coat having an hydroxyl containing acrylic resin crosslinked with diisocyanates and melamine formaldehyde. The clear coat appears to be separating into layers, and fracturing of the ring can be observed. This is a result of the dew being absorbed into the paint coating followed by the dew reacting with the paint surface. As the dew reacts with the clear coat, the elasticity of the paint coating decreases resulting in splitting of the surface. The ring shaped form of the damage suggests a free energy minimization process favoring a concentration of the damaging reagent at the edge of the evaporating drop. This process will be discussed in a separate section of this paper.

Scanning Electron Microscopy Observations

Scanning Electron Microscopy permitted the obtaining of qualitative sulfur concentrations on the surface of the damaged areas through X-ray compositional sulfur mapping. Damage to a paint with a clear coat composed of an acrylic resin containing hydroxyl groups, modified with a polyester resin and crosslinked with melamine formaldehyde observed using SEM is shown in Figure 2. To the left is a sulfur mapping of the damaged area. The lighter a particular part of the map, the higher the concentration of sulfur (probably in the form of SO_4^{2-}) in that particular part of the damage area. On the right is an image of the damaged area. The part of the image indicated by arrows is not a damaged area, but is a scratch identification mark. Deposition of sulfur is generally located in a central area. These samples were rinsed and buffed after exposure, so either the sulfur had chemically combined with the paint, or was in some other form resistant to buffing.

Profilometry Observations

Profilometry was also used to assess damage levels. This technique can give quantitative comparison of damage amounts between samples since it measures the actual size (width, height, or depth) of the damaged areas. Unfortunately, due to the unevenness of the paint coatings, the background noise was high which limited the precision and usefulness of this technique for studying the samples. Figure 3 shows a profile of damage formed on a paint

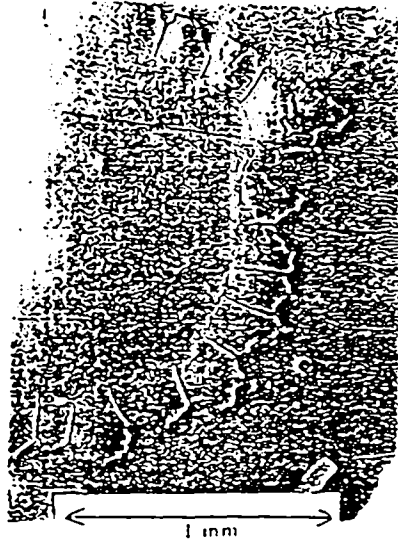


Figure 1 Chamber Dew #7 Damage - Paint #2
50 Minute Exposure at 54°C

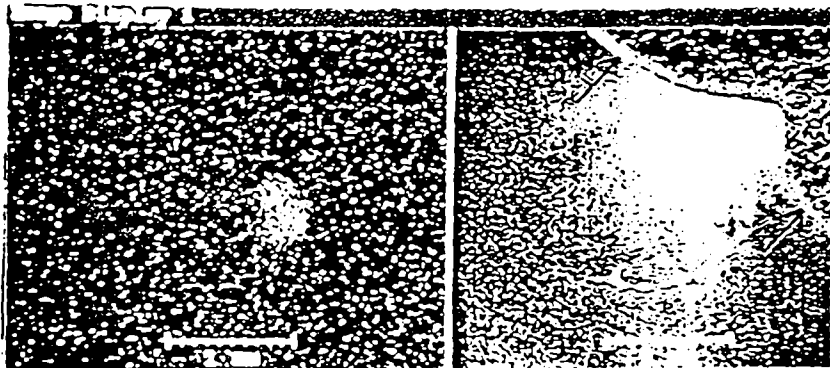


Figure 2 Chamber Dew #6 Damage - Paint #7
50 Minute Exposure at 54 C
(EDS Sulfur map on left; Photomicrograph on right)
(Arrows indicate scratch marks for identification of damage location).

with a clear coat having an acrylic resin containing hydroxyl groups and crosslinked with diisocyanates. A crater shaped blister was formed with wall heights up to 0.6 micrometers.

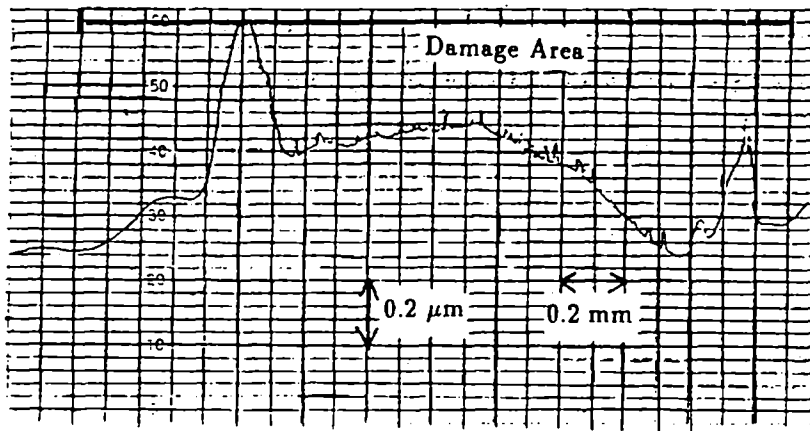


Figure 3 Profile of Chamber Dew #7 Damage - Paint #4
50 Minute Exposure at 54 C

Results from inspection of the profilometer analysis and photomicrographs of the exposed paints indicate that the damage areas are not necessarily etches as would be expected from acid attack. What seems to be occurring is instead a separation of the clear coat into layers. The acidic dews at elevated temperatures generally form an uplifted crater on the paints. The center of the crater is approximately the same height as the rest of the paint. However, the sides of the crater are higher than the rest of the paint.

Chamber Dew Evaporation Process on Paint Surface

Visual observations of the evaporation process of the chamber dews on the paint surfaces show that no change of the clear coat surfaces of the paints tested occurs until a critical drop size is reached. At this critical size, deposition of material from the drop begins and continues until the drop has completely evaporated. After this evaporation, an area of deposition can be observed which is much smaller than the initial drop size with the highest levels of deposits located in a circular ring. After washing and buffing, a circular ring of damage is observed which is located at the same places on the surface where deposits were formed.

Deposition of material from the reagent drop occurs only after the drop reaches a critical size or concentration. Once this concentration is reached, precipitation occurs, resulting in material being deposited on the paint surface with the highest levels occurring at the edge of the drop. This location appears to be the most favorable for the creation of nucleating centers of the depositing material to form. Favorable locations for nucleation in solutions occur at the surface of solutions (the drop surface in our case), or at the walls of the vessel containing the solution (the drop-paint interface in our case)⁴. These locations

are favorable because the interfacial free energy of a nucleating center is lowered in these locations. A nucleus located at the edge of the drop exists at both favorable locations simultaneously, resulting in a further decrease in the free energy of formation compared with either location alone or the interior of the solution.

CONCLUSIONS

The results from these investigations indicate that acid deposition causes considerable damage to automotive coatings with clear coat surfaces. The chamber dews formed uplifted craters on the paints. The center of the crater is approximately the same height as the rest of the paint, but the walls are higher. The visual damage on the paint surface appeared to occur as a result of the interaction at elevated temperature between the deposited material from the evaporated drop and the clear coat surface with the damage levels on the paint surface increasing as the time of heating increased. The ring shaped damage produced by the dews appeared to be a result of a nucleation process which favored the deposition of the damage producing material at the edge of the evaporating drop.

Reflection microscopy, scanning electron microscopy, and profilometry were found to be useful techniques to evaluate the damage on the paint surfaces. Reflection microscopy and profilometry were helpful in determining the physical structure of the damage to the paint surface. Scanning electron microscopy was most useful for obtaining sulfur mapping of the paint surfaces through the use of an EDS attachment to the SEM.

REFERENCES

1. G. T. Wolff, W. R. Rodgers, D. C. Collins, M. H. Verma, and C. A. Wong, "Spotting of Automotive Finishes from the Interactions Between Dry Deposition of Crustal Material and Wet Deposition of Sulfate," J. Air Waste Manage. Assoc. 40(12): 1638-1648(1990).
2. T. C. Simpson and P. J. Moran, The John Hopkins University, Baltimore, MD, personal communication, 1990.
3. J. White and W. Rothschild, "Defects in the Finish of Motor Cars," Metal Finishing 85(5): 15-18 (1987).
4. D. Elwell and H. J. Schell, Crystal Growth from High-Temperature Solutions, Academic Press, London, 1975, p.100.

DISCLAIMER

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