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SOILING, CLEANING, AND WEATHERING EFFECTS ON AIRCRAFT POLYURETHANE TOPCOATS

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Weathering caused slight erosion and chalking of the polyurethane topcoat surfaces. Periodic cleaning of weathered specimens removes part of this eroded surface and provides a slightly restoring effect. Accelerated weathering in a xenon arc weathering chamber for 1600 hours caused cracking of MIL-C-83286 topcoats. The polymer bead coatings did not crack during this exposure, however they did significantly erode across the surface and primarily around the polymer bead particles.

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PREFACE

Under the Navy Exploratory Development Program for Airborne Materials, a project was undertaken to study the cleanability and weatherability of aircraft camouflage coating systems. The following is a phase report which discusses weathering, soiling, and cleaning effects on polyurethane topcoats. During this project, commercially available coatings which qualify under military specifications were analyzed. Discussion pertaining to these products in this report does not imply or otherwise constitute an endorsement by the authors or the U.S. Government.

INTRODUCTION

Navy aircraft paint systems consist of an epoxy primer (MIL-P-23377 or MIL-P-85582) and a polyurethane topcoat (MIL-C-83286). The topcoat is a two component, aliphatic polyurethane which is the product of a polyester polyol and hexamethylene diisocyanate. U.S. Navy operational aircraft utilize a multi-theater camouflage scheme consisting of several lusterless gray topcoats. Although this coating system is considered to be the premier finishing system for corrosion prevention and combat survivability of aircraft, one of the most frequently reported aircraft maintenance problems is poor cleanability (soil retention), which causes degradation of the coating and difficulty in color matching during touch-up.

Reference 1 discusses the cleanability of several polyurethane topcoats used on Navy aircraft. In summary, the results show a distinct correlation between coating cleanability and 60° gloss. As illustrated in Figure 1, topcoats with a gloss of less than 4 had significant color changes when soiled and cleaned while coatings with gloss values above 4 had color changes which were far less noticeable even after 10 soiling/cleaning cycles. (Note: Change in coating color was determined by measuring L,a,b color values prior to and after exposure, represented by i and f, respectively. The color change was then calculated by:

$$dE = \sqrt{(L_f - L_i)^2 + (a_f - a_i)^2 + (b_f - b_i)^2}$$

The higher dE is, the greater the color change and the poorer the coating cleanability.) The effect observed in Figure 1 is caused by the surface roughness required for low gloss coatings, allowing carbonaceous soil particles to become entrapped in the coating surface. A second trend was found with the hydrophilic nature of the coating surface and cleanability. As suggested in Figure 2, coatings which were more hydrophilic (lower contact angle) were more cleanable than those which were hydrophobic. This effect is attributed to the smoother surface of the hydrophilic coatings and the ability of the cleaner to wet these surfaces more efficiently. Reference (1) also discusses the improved cleanability of low gloss (<3) coatings which contain polymer bead pigments. The bead coatings have a thin layer of resin which coats the surface, and rounded surface protrusions while conventionally pigmented topcoats of equivalent gloss (1.0) were resin starved at the surface and had jagged surface protrusions. This effect is illustrated in the scanning electron micrographs in Figure 3. The surface exhibited by the polymer bead coatings was far less

likely to entrap and retain soil particulates.

The study described in reference (1) was performed on laboratory specimens which were unexposed to weathering elements: radiation, rain, and humidity. Over time, these conditions significantly change the chemical nature of the coating, especially at the surface, and effect coating cleanability. The effort described in this report is a study of the synergistic effects of weathering, soiling, and cleaning on lusterless aircraft polyurethane topcoats.

EXPERIMENTAL

The coatings evaluated during this study were MIL-C-83286, "COATING, URETHANE, ALIPHATIC ISOCYANATE, FOR AEROSPACE APPLICATION", qualified materials provided by Deft and DeSoto. A polyurethane topcoat (DeSoto) containing polymer bead pigments, which is applied to production F/A-18 aircraft, was also studied. The color of these topcoats was Federal Standard 595: 36320, which is one of the colors used in U.S. Navy aircraft multi-theater camouflage schemes. The 60° gloss of these coatings after application and cure was approximately:

<u>MANUFACTURER</u>	<u>GLOSS</u>
Deft	3.6
DeSoto	1.1
DeSoto-Camolite	1.1

The substrate specimens, coating application procedure, gloss, color, cleanability, and water contact angle procedures are described in Reference (1). The accelerated weathering exposures were performed in a 6000 watt, xenon arc weatherometer. The continuous cycle consisted of 102 minutes of high intensity light only and 18 minutes of light and water spray. The specimens were tested according to ASTM method G26, Type BF with the conditions in the chamber as follows:

Black body temperature	$140 \pm 5^{\circ} \text{ F}$ ($60 \pm 3^{\circ} \text{ C}$)
Relative humidity	$50 \pm 5\%$
Intensity of the arc	0.55 ± 0.05 watts per square meter at 340 nanometers wavelength

RESULTS AND DISCUSSION

In order to determine the effects of weathering on coating cleanability, the three aircraft polyurethane topcoats were systematically subjected to three separate conditions:

- (1) Accelerated weathering for 1600 hours.
- (2) Accelerated weathering, while cleaning at 200 exposure hour intervals (total of 1600 hours exposure and 8 cleanings).
- (3) Accelerated weathering, with soiling and cleaning at 200 exposure hour intervals.

Changes in coating color and gloss were characterized at 200 hour intervals. Changes in the coating hydrophilicity and topography were examined by measuring the contact angle of water and studying SEM's before and after exposure.

Figures 4, 5, and 6 illustrate the change in color, dE, versus exposure time for the three coatings during weathering, weathering/cleaning, and weathering/soiling/cleaning, respectively. Figures 7 through 10 are SEM's of the three coatings at 500X and 2000X after weathering and weathering/soiling/cleaning exposures. Weathered/cleaned specimens were also analyzed using the electron microscope and had a similar appearance to the weathered/soiled/cleaned specimens.

During the weathering and weathering/cleaning conditions, the change in color was relatively negligible for all three coatings. However, two noticeable trends in the data were observed. In both the weathering and weathering/cleaning (Figures 4 and 5), the relative color change between the three coatings was the same: Camolite, DeSoto, and Deft in increasing order of color change. The colorfastness of Camolite agrees with previous literature (2-6) which claims good weather resistance due to the polymer bead stability. However, SEM's of this coating (Figures 7C and 8C) clearly indicate an erosion of the polymer bead coating surface due to weathering. Color stability in this case is probably caused by the erosion of the coating surface, exposing a fresh pigmented surface which matches the color of the original surface. The DeSoto coating color diverges less than the Deft coating and this is attributed to the pigment rich surface of the DeSoto coating which also can easily erode and chalk, exposing a fresh surface. The SEM's in Figures 7B and 8B confirm that the surface is changing. Comparing these figures with SEM's of the unexposed DeSoto coating (Figure 3B), it is obvious that the exposed specimens are not as rough and some of the original surface has been removed. The erosion/chalking mechanism is frequently designed into exterior coatings, especially house paints, so that they maintain their original color. The Deft coating has a thin layer of resin over the surface (Figures 3A, 7A, and 8A) which can discolor and, without the erosion/chalking process, restoration of the surface is not possible and a color change will occur and remain as is observed. It must be noted that although a color change trend was observed for weathered and weathered/cleaned specimens, the magnitude of color change was not significant relative to the soiled specimens which will be discussed later in this report.

The second noticeable trend of the data in Figure 5 is the slight reversion of the coatings back to their original colors when periodically cleaned during the weathering cycle. The extent of this effect is demonstrated more clearly in the three graphs present in Figure 11 which directly compare weathered and weathered/cleaned specimens. The improvement in color is attributable to the cleaning action removing the uppermost layer of the coatings which have discolored slightly. Thus, a fresh pigmented surface is exposed. SEM's of weathered versus weathered/cleaned specimens confirm that the cleaning action removes the directly exposed upper surface, revealing fresh surface which is more representative of the original color.

Figure 6 illustrates the results for specimens which were weathered/soiled/cleaned. The effect of soil on color change is evident in the magnitude of dE. This is also clear in the data presented in Figure 12,

comparing "LOG (dE)" for the weathered and weathered/soiled/cleaned coatings. All three coatings exhibit a significant color change after the first soiling/cleaning cycle performed at 200 hours exposure. The dE values are 3.3, 6.7, and 12.7 for the Deft, Camolite, and DeSoto coatings, respectively. As the coatings continue through the weather/soil/clean cycle, dE significantly increases. The performance trend between the coatings when soil is introduced into the cycle is different than those observed in Figures 4 and 5 and this effect is attributed to the different surface roughness characteristics of the three coatings. As described previously and in reference (1), the DeSoto coating has a gloss of 1.1 with a rough, pigment rich surface. The Camolite coating has a gloss of 1.1 but the surface is not quite as rough, having a thin layer of resin over the pigment particles. The Deft coating has a gloss of 4 with a smoother, more consistent surface. A rougher surface entraps more dirt, having a greater effect on color change which explains the difference in coating cleanability indicated in Figures 11 and 12. It should be noted that the average particle diameter of the carbon particles used in the soil was approximately 0.02 microns which is not discernible by magnitudes possible with an SEM.

Analysis of the exposed coatings using the SEM provided three unexpected observations which have not been reported in previous literature and deserve discussion:

- (1) A difference in the topography of the conventionally pigmented (Deft and DeSoto) coatings before exposure, after weathering, and after weathering/soiling/cleaning.
- (2) Significant cracking of these "weather resistant" polyurethanes upon exposure to accelerated weathering.
- (3) Erosion of polymer bead coatings which previously have been reported to be extremely weather resistant and inert (2-6).

The SEMs of unexposed, weathered, and weathered/soiled/cleaned topcoat specimens indicate that the Deft coating undergoes no drastic changes in topography (with the exception of cracking which will be discussed below). However, weathered and weathered/soiled/cleaned coatings appear to be slightly rougher than the unexposed specimens. This suggests some minor erosion/chalking has occurred which effects the thin layer of resin on the surface, exposing more pigment.

SEMs at 2000X of the DeSoto coating show some differences between the unexposed and weathered/soiled/cleaned specimens. The unexposed specimen is extremely rough with a resin starved surface, exposing pigment. It has a surface roughness on the magnitude of 5 to 10 microns, but also a microroughness at the sub-micron level. The weathered specimen exhibits very little of the sub-micron irregularities. This is probably caused by the "rinsing" action in the weathering cycle which removed any loose debris from the surface. The weathered/soiled/cleaned specimen appears slightly smoother than the weathered specimen, caused by the burnishing action of the cleaning cycle.

Figures 7 through 10 show obvious cracking of Deft and DeSoto MIL-C-83296 polyurethane topcoats upon accelerated weathering in a xenon arc weatherometer. This was unexpected since MIL-C-83286 has an accelerated weathering exposure

requirement of 500 hours with minimal reduction in flexibility. It is suspected that these cracks are caused by internal stresses arising from chemical and surface changes in the coatings during weathering. Although the 1600 hour exposure period of this study significantly exceeds the specification exposure period, it may be a reasonable duration for evaluation of coatings for Navy aircraft which are repainted approximately every 4 to 6 years. During that service time, they are exposed to extremely harsh environmental conditions: sunlight, wide temperature ranges in flight (-65° to 350°F) and on ground ($<0^{\circ}$ to $>100^{\circ}\text{F}$), high humidity, salt spray, and carbonaceous oily soils. In order to further understand cracking and other aircraft polyurethane coating responses to weathering, an extensive study has been initiated which will examine chemical, physical, optical, and surface property changes of the coating during exposure in Florida, a xenon arc weatherometer and a QUV chamber (ASTM G-53).

The third significant observation from the SEMs is the effect of weathering on the polymer bead coating, Camolite. Although it did not crack, the coating appears to be eroded across the entire surface but more dramatically around the polymer bead particles. This also was unexpected. Previous reports on polymer bead coatings specifically discuss the weather and chemical resistance of aircraft polyurethane coatings containing these pigments (2-6). Other references discuss gloss uniformity, scrub resistance, opacity, application characteristics (7), and light scattering effects (8) imparted by polymer beads when incorporated into a paint binder. It should be noted that although the method of bead preparation was similar in these studies (9), the bead manufactureres were different. Nonetheless, the effect of weathering on the Camolite coating in this study is obvious. One explanation of the degradation mechanism is that the beads, which are normally produced from a styrenated polyester, are susceptible to ultraviolet degradation due to the small concentration of the aromatic segment in the copolymer. Further evaluation of this effect is ongoing.

Although there were slight variations in gloss measurements for all three coatings during the three exposure conditions, there was no significant change in gloss for any of the coatings. This is exemplified in Figure 13 with the gloss data obtained for the Deft material.

Contact angles of distilled water on the coatings' surface were measured before and after the three exposure conditions. These results are presented in Table I. The initial contact angle for the DeSoto coatings is highest, followed by Camolite and Deft coatings, respectively. This can be attributed to the descending order of surface roughness of the three coatings. The results clearly indicate that simply weathering the three coatings will lower the contact angles, and as indicated in reference 1, cleaning the unsoiled coatings will also lower the contact angles, rendering the surface more hydrophilic. When soil was introduced to the cycle, the Deft and Camolite coatings illustrated slightly higher contact angles, but the contact angle for the DeSoto coating was significantly higher. This is attributed to the rough surface of the DeSoto coating, confirmed in the SEM's, retaining soil which is hydrophobic.

The importance of these contact angle measurements is significant when considering the conclusion of previous work (1) that more hydrophilic surfaces are less likely to retain soil. This conclusion was confirmed in the current study by soiling and cleaning weathered and weathered/cleaned specimens. The change in color of these coatings was far less than that observed for virgin

coatings. If applied coatings are permitted to weather without soiling for a period long enough to render them more hydrophilic, they are likely to be more cleanable. In many cases Navy aircraft are prematurely flown after being freshly painted; therefore, weathering of these repainted aircraft would also provide more time for the coating system to cure, which would enable it to perform better. In addition, a lowering in the contact angle indicates a decrease in the surface energy of the coating (10), thus indicating a change in the surface chemistry. This effect is currently being investigated in greater detail.

Table I: Contact Angles of Distilled Water on Polyurethane Coating Surfaces

<u>CONDITION</u>	<u>DEFT</u>	<u>DESOTO</u>	<u>CAMOLITE</u>
Original	74.0	98.0	81.0
Weathered	51.0	66.0	33.7
Wea/Clean	39.3	46.0	36.0
Wea/Soil/Clean	41.3	76.0	41.3

In an operational environment, such as on an aircraft carrier, aircraft are not usually cleaned immediately after they are soiled. In contrast, the soiling process is continuous. Navy aircraft are required to be washed approximately every two weeks during normal operating conditions. Even at this interval, soiled and contaminated surfaces are exposed to environmental conditions of sunlight, high humidity, sea spray and elevated temperatures. In order to determine the effects of these conditions on the tenacity of soil, specimens were soiled as described in reference (1) prior to any other conditioning. Three control specimens were cleaned immediately, the remainder of the specimens were exposed in the xenon arc accelerated weathering environment. Panels were removed after 1, 2, 4, 7, and 10 days exposure and immediately cleaned. The results are presented in Figure 14 as dE color change versus days exposed to accelerated weathering after soiling. This data indicates that soil is definitely more tenacious after it is exposed to environmental conditions. This effect is easily explained considering:

- (1) Elevated temperatures, humidity, and ultraviolet radiation will degrade the coating's polymeric surface.
- (2) The soil contains carbon black particles which are known to have a chemically active surface (11).

With these two conditions present, it is likely that the carbonaceous particles were not only embedded in the coating surface but also reacted with the polymeric binder. Therefore, it would appear that the more frequently a surface is cleaned, the less time is permitted for this action to occur, and the more likely to restore the coating to its original condition.

CONCLUSIONS

1. Color change of the polyurethane topcoats during weathering and weathering/cleaning was negligible. Color change when specimens were weathered, soiled, and cleaned was significant, especially for low gloss topcoats. However, polymer bead coatings of equivalent gloss (1.1) to conventionally pigmented camouflage coatings performed better, undergoing less color change.
2. None of the three exposure conditions, weathered, weathered/cleaned, and weathered/soiled/cleaned, significantly changed the gloss of the coatings analyzed.
3. All three exposure conditions caused the coatings' surface to become more hydrophilic. Topcoats which were weathered and weathered/cleaned were more cleanable after soiling than their unexposed counterparts because of their hydrophilic surface.
4. Weathering caused slight erosion and chalking of the polyurethane topcoat surfaces. Periodic cleaning of weathered specimens removes part of this eroded surface and provides a slightly restoring effect.
5. Accelerated weathering in a xenon arc chamber for 1600 hours caused cracking of MIL-C-83286 topcoats. The polymer bead coatings did not crack during the exposure, however they did significantly erode across the surface and primarily around the polymer bead particles.
6. Weathering of a soiled surface makes the soil much more tenacious and difficult to remove.

RECOMMENDATIONS

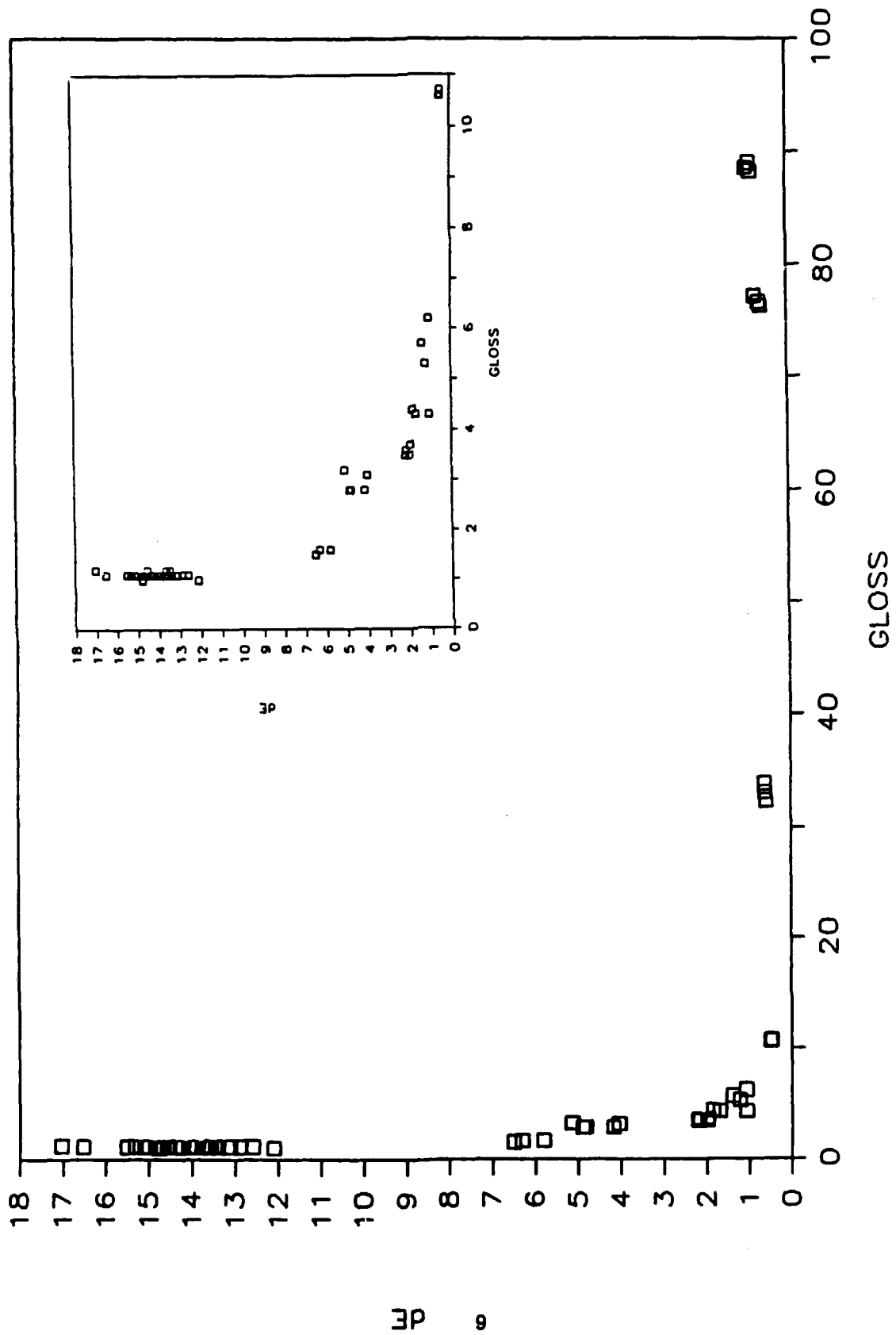
1. Topcoats on freshly painted aircraft should be made more hydrophilic to improve their cleanability. One such process is to expose them to the outdoor environment shortly after the paint has cured and hardened, and then clean them after several days exposure.
2. Operational aircraft should be cleaned as often as possible, especially in high exhaust impingment areas.
3. Conventional and polymer bead aircraft coatings should be fully characterized for natural and accelerated weathering effects.
4. Aircraft topcoats which are less susceptible to soil retention and color change during operational conditions should be developed.

ACKNOWLEDGEMENT

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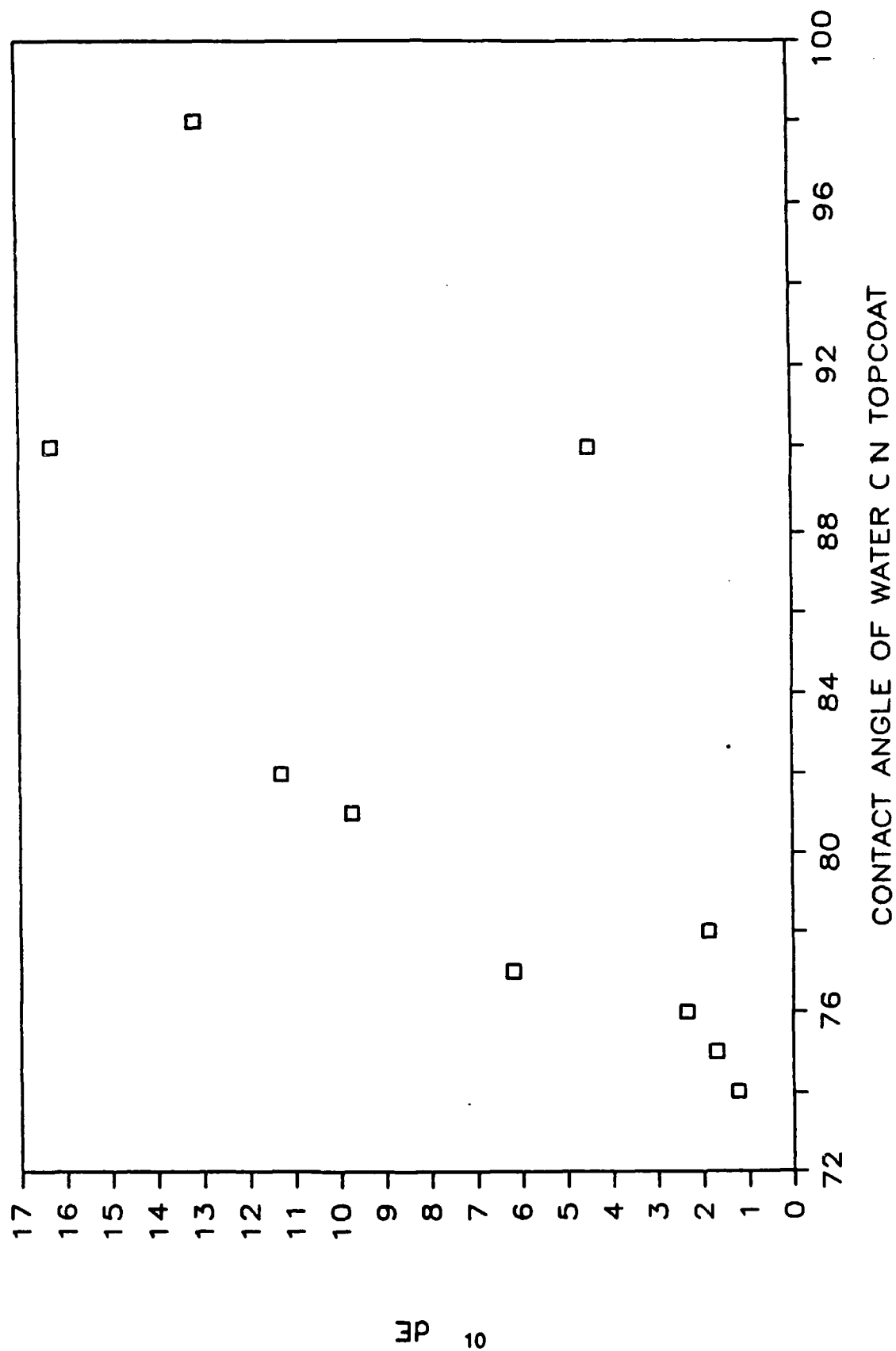


FIGURE 2. COLOR CHANGE, dE, VERSUS CONTACT ANGLE OF WATER ON POLYURETHANE AIRCRAFT TOPCOATS

TOPOGRAPHY OF POLYURETHANE TOPCOATS - SEM

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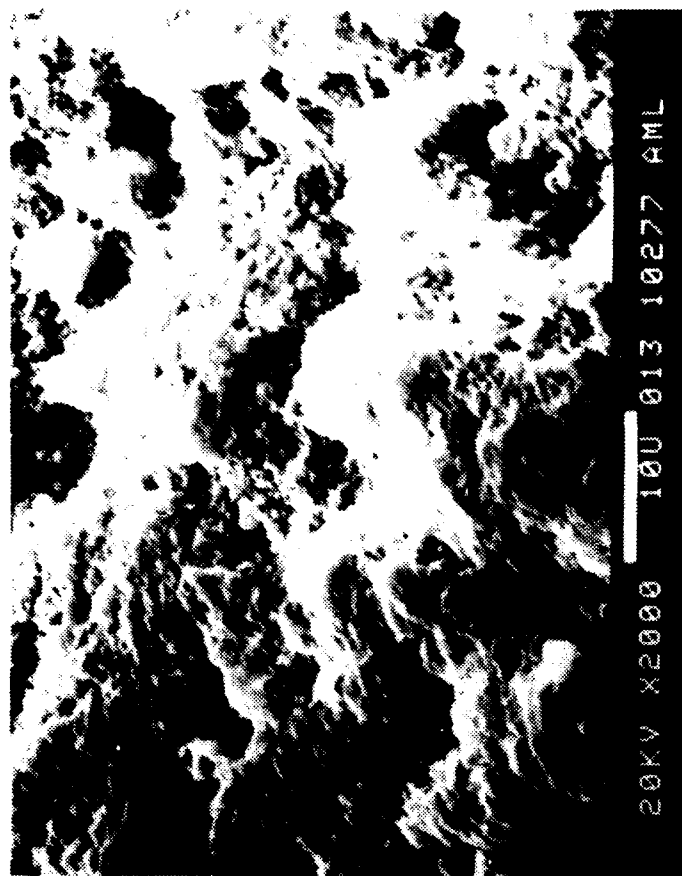


FIGURE 1. SCANNING ELECTRON MICROGRAPHS (2000X) OF POLYURETHANE AIRCRAFT TOPCOATS

- A. DEFT
- B. DESOTO
- C. CAMOLITE

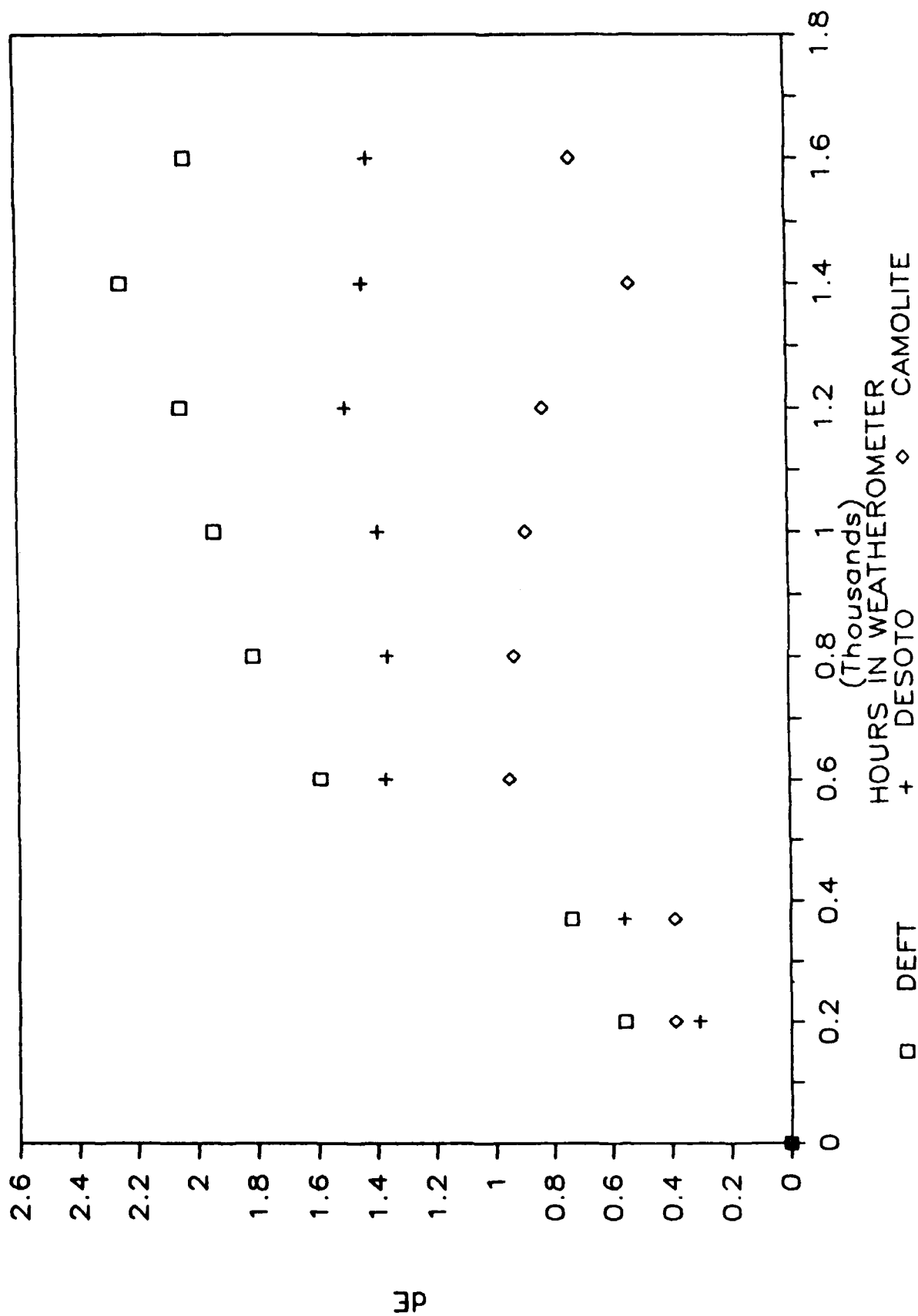


FIGURE 4. COLOR CHANGE, dE , VERSUS HOURS IN WEATHEROMETER

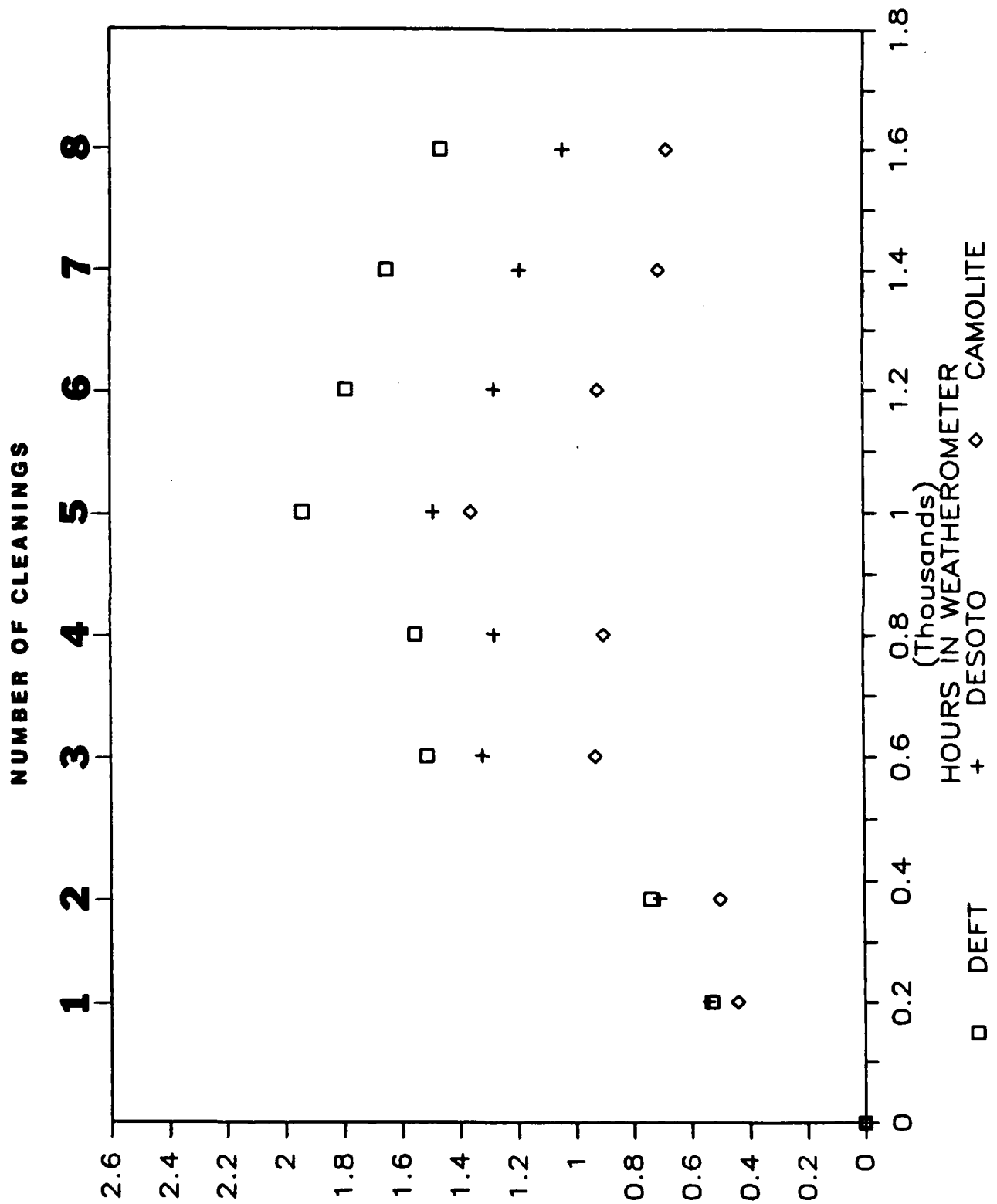


FIGURE 5. COLOR CHANGE, dE, VERSUS HOURS IN WEATHEROMETER FOR WEATHERED/CLEANED TOPCOATS

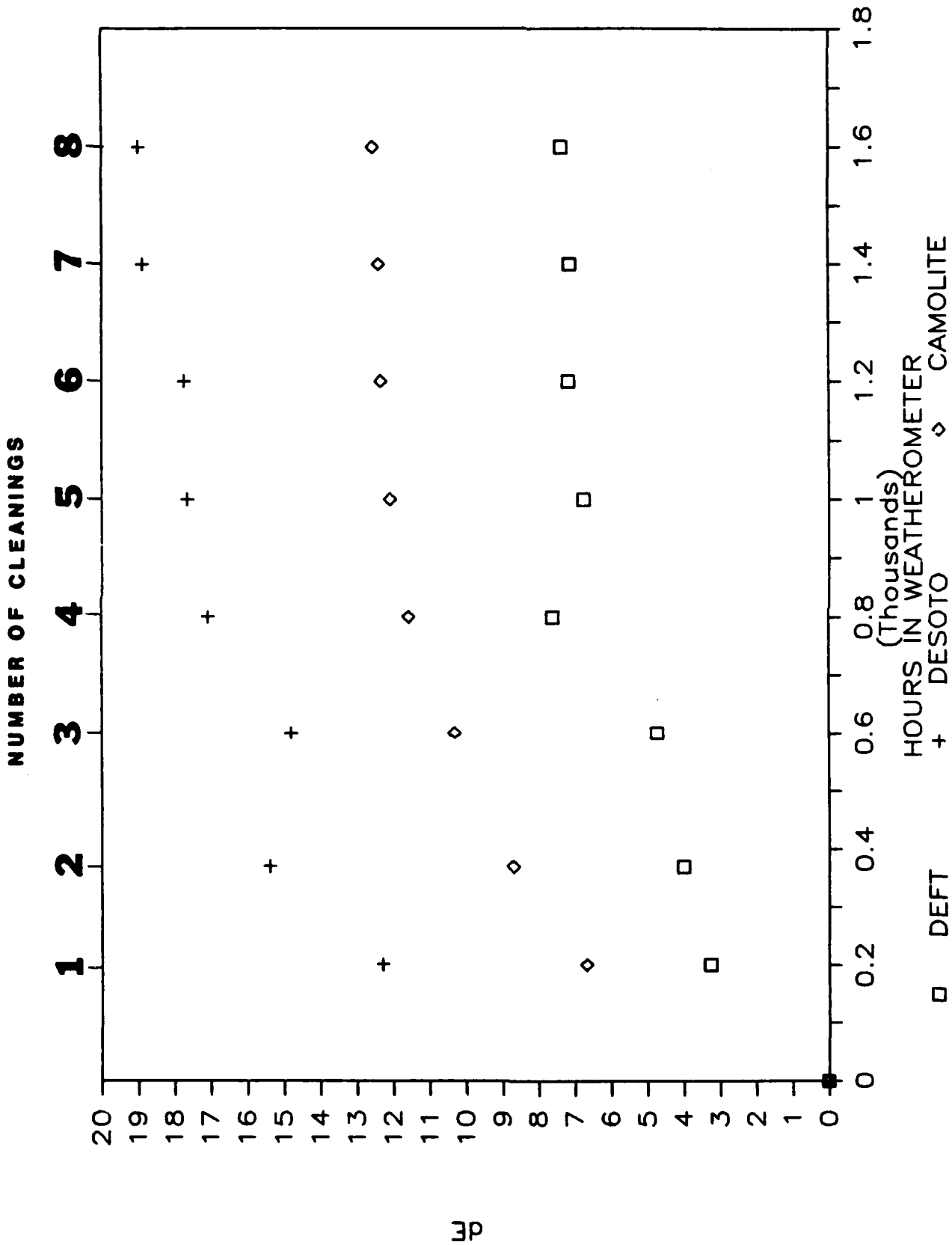


FIGURE 6. COLOR CHANGE, dE , VERSUS HOURS IN WEATHEROMETER FOR WEATHERED/ SOILED/CLEANED TOPCOATS

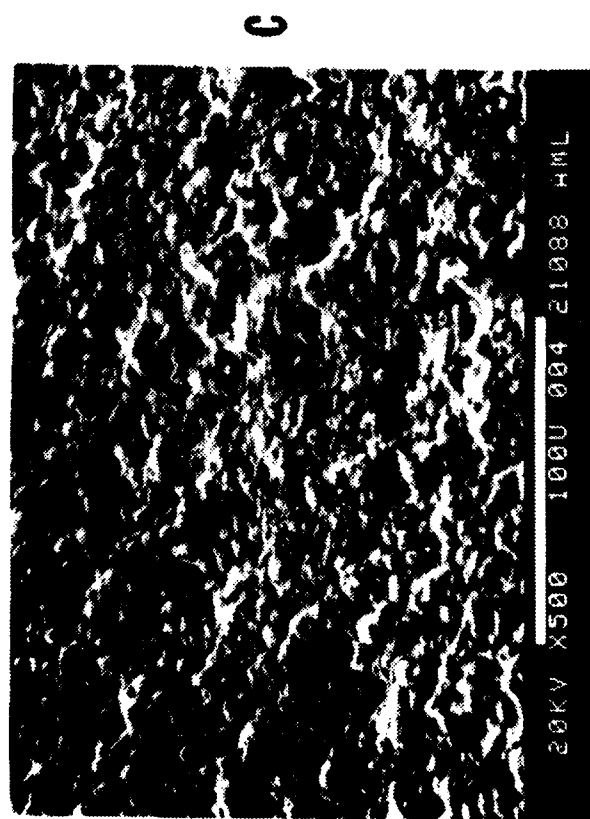
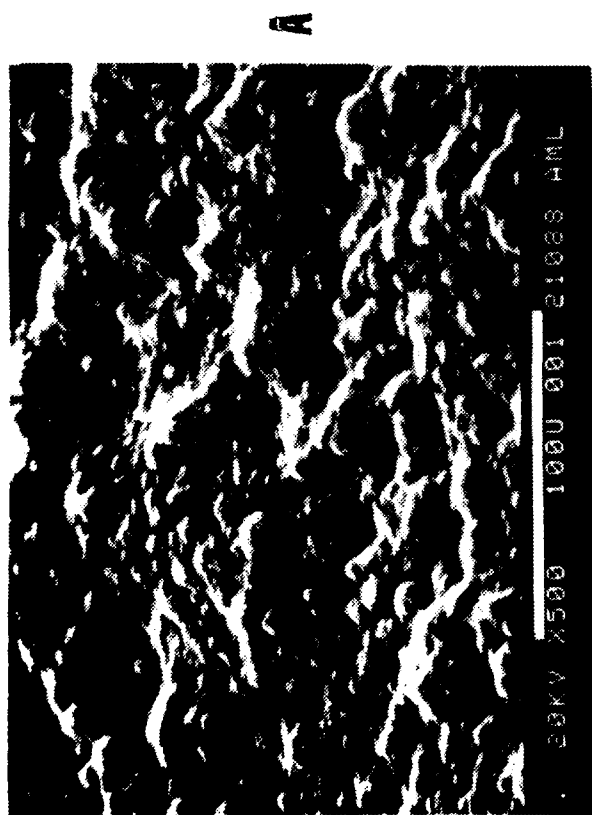
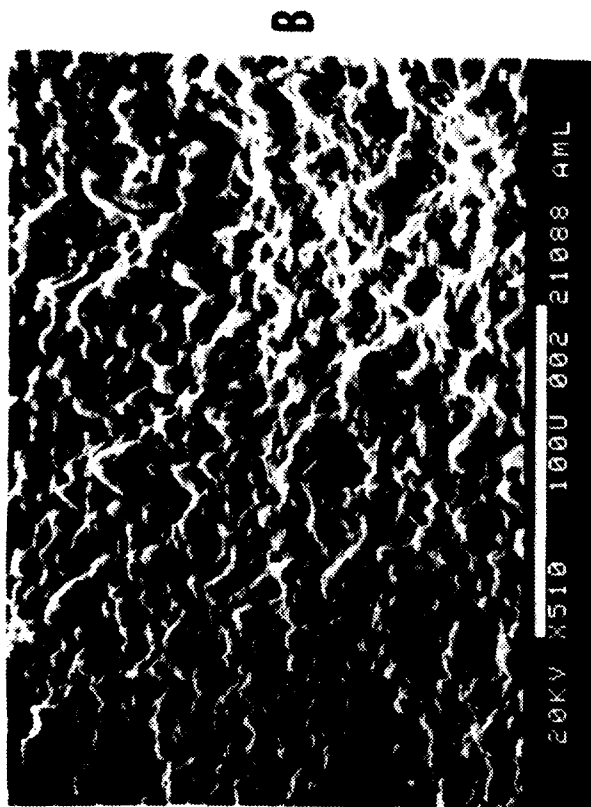


FIGURE 7. SEMs (500X) OF WEATHERED SPECIMENS

- A. DEFT
- B. DESOTO
- C. CAMOLITE

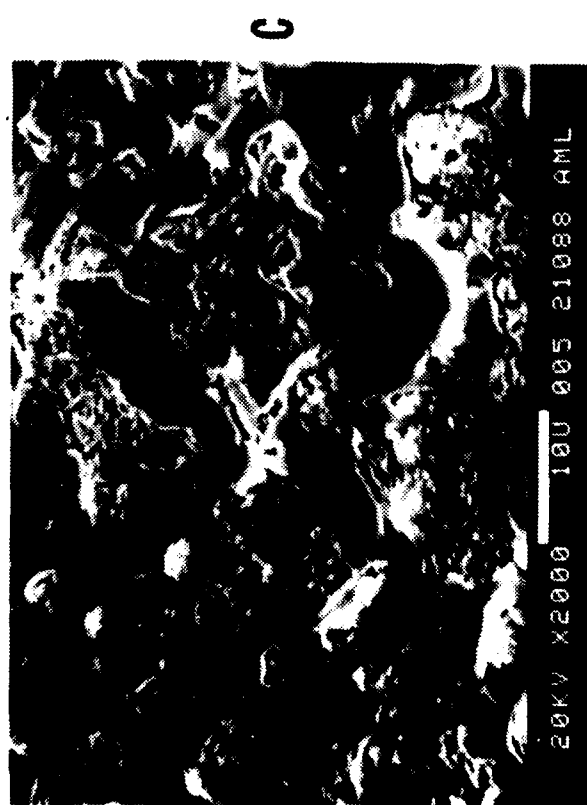
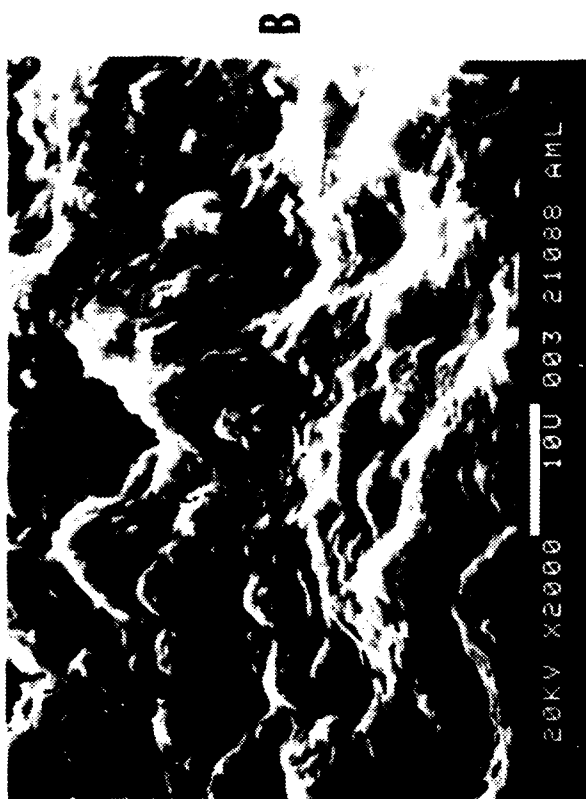


FIGURE 8. SEMs (2000X) OF WEATHERED SPECIMENS

- A. DEPT
- B. DESOTO
- C. CAMOLITE

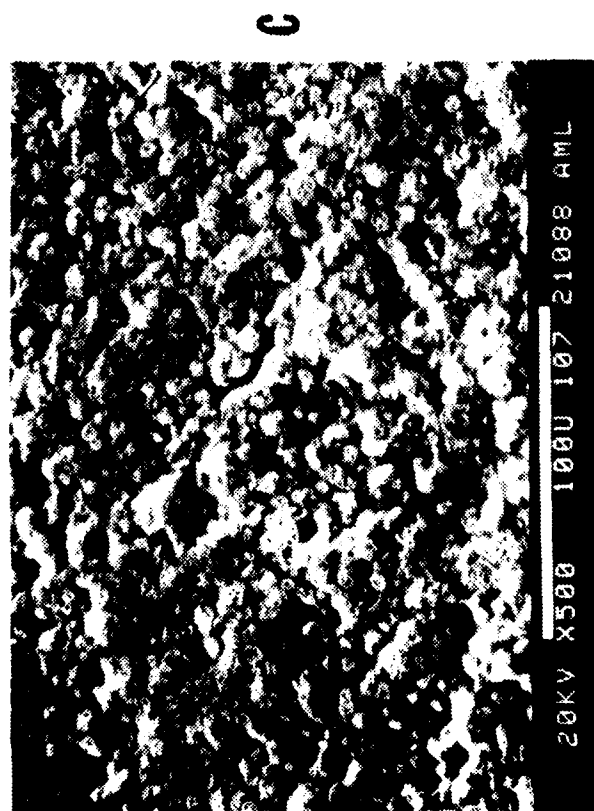
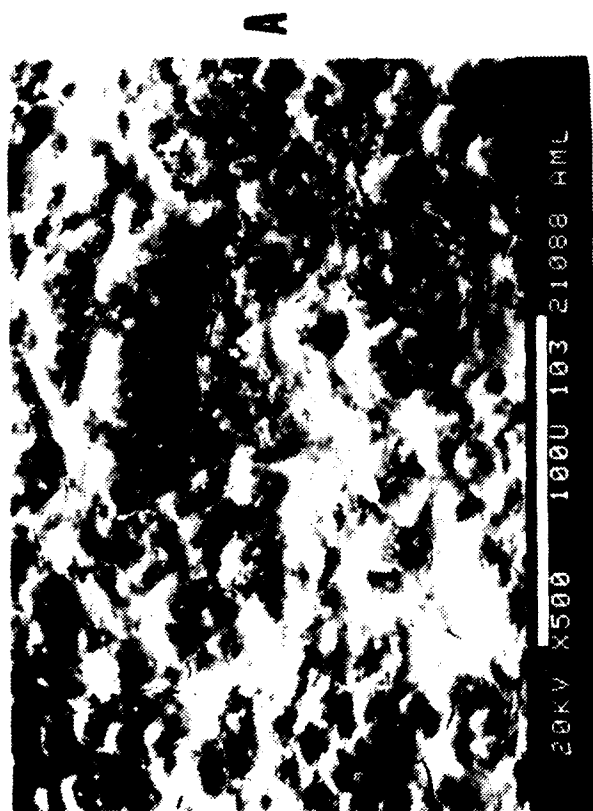
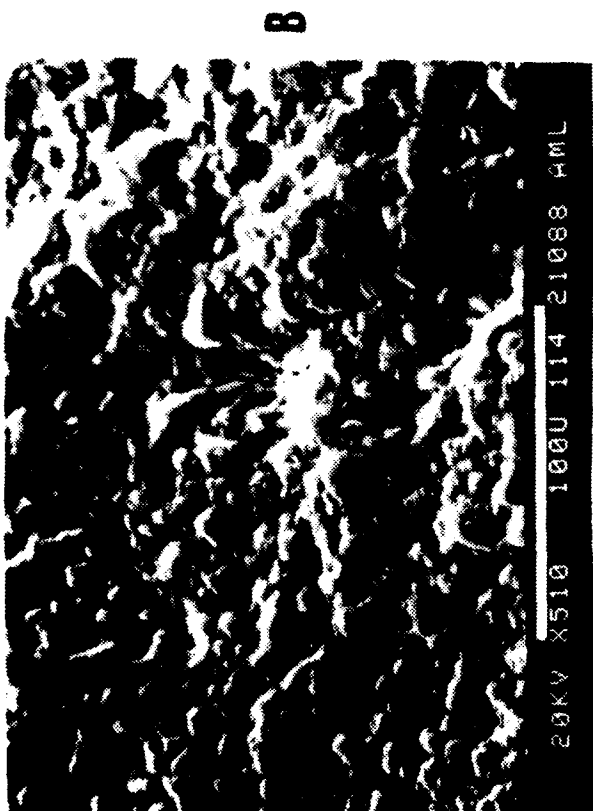


FIGURE 9. SEMs (500X) OF WEATHERED/SOILED/
CLEANED SPECIMENS

- A. DEFT
- B. DESOTO
- C. CANOLITE

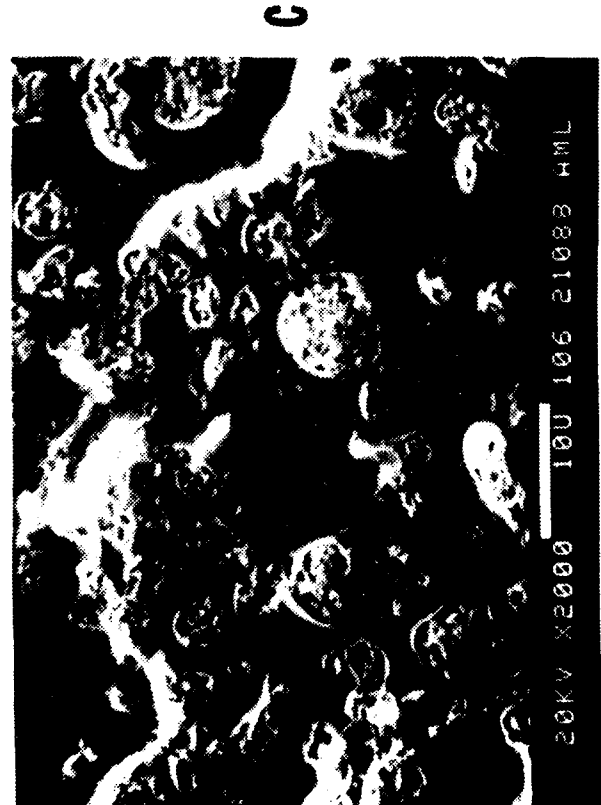
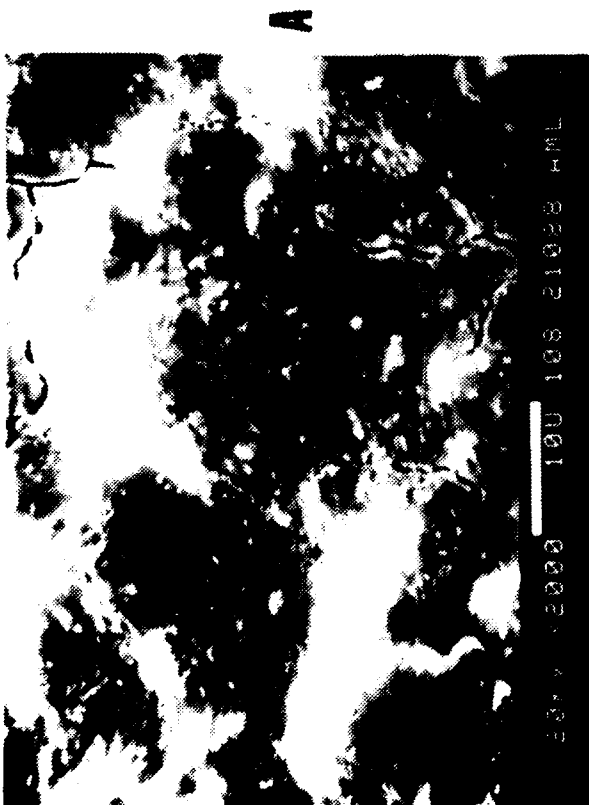
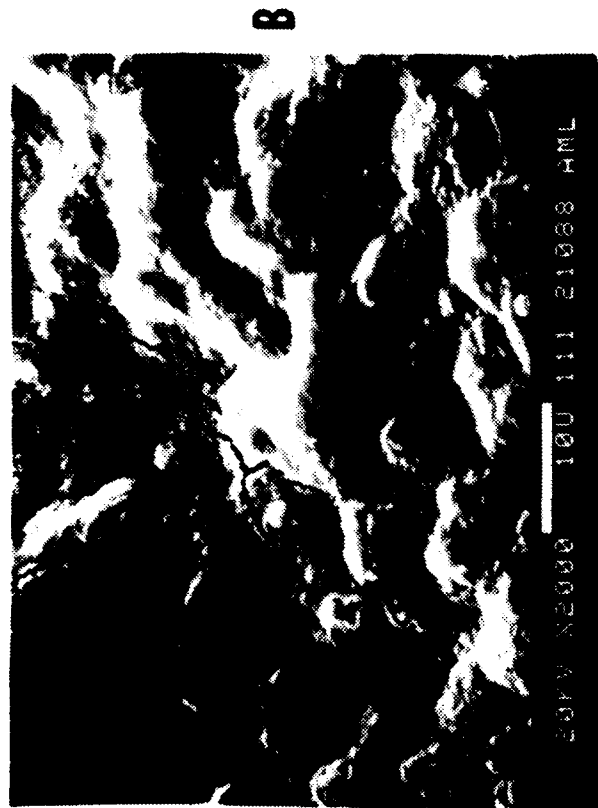


FIGURE 10. SEMs (2000X) OF WEATHERED/SOILED/
CLEANED SPECIMENS

- A. DEFT
- B. DESOTO
- C. CAMOLITE

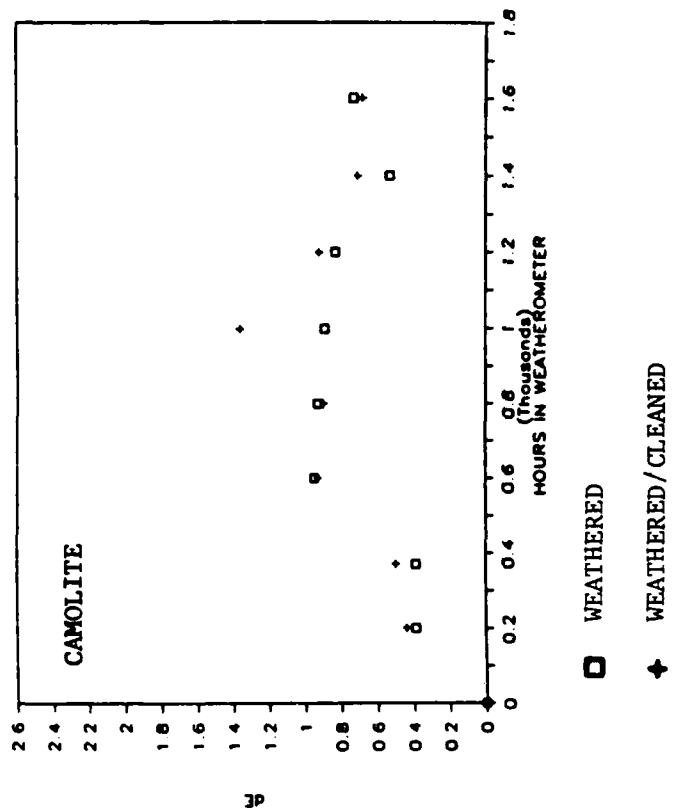
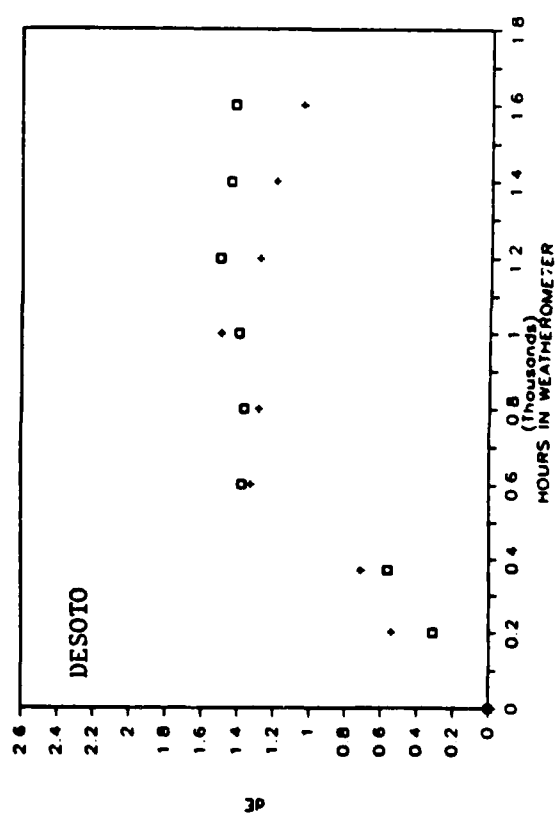
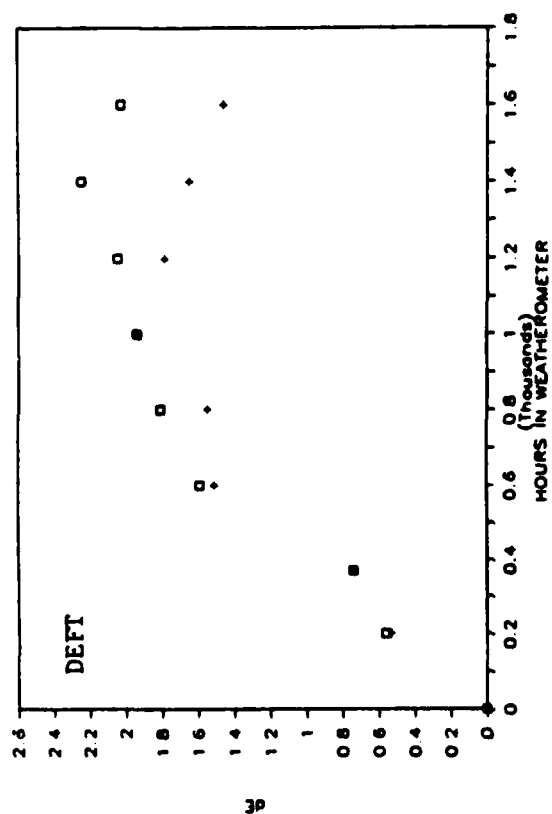


FIGURE 11. COMPARISON OF COLOR CHANGE, ΔE , VERSUS HOURS IN WEATHEROMETER FOR WEATHERED AND WEATHERED/CLEANED SPECIMENS



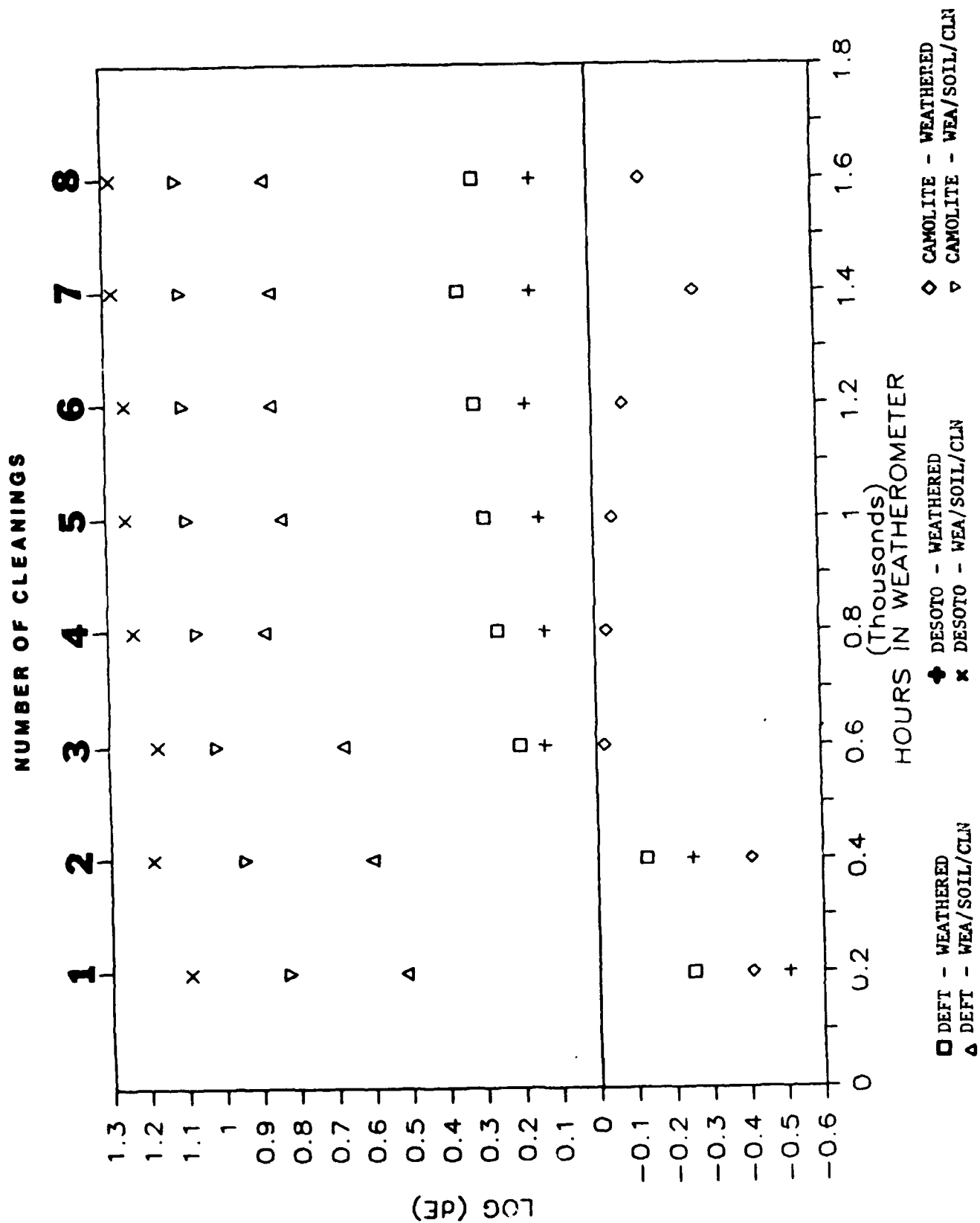


FIGURE 12. COLOR CHANGE, LOG DE, VERSUS HOURS IN WEATHEROMETER FOR WEATHERED AND WEATHERED/SOILED/CLEANED SPECIMENS

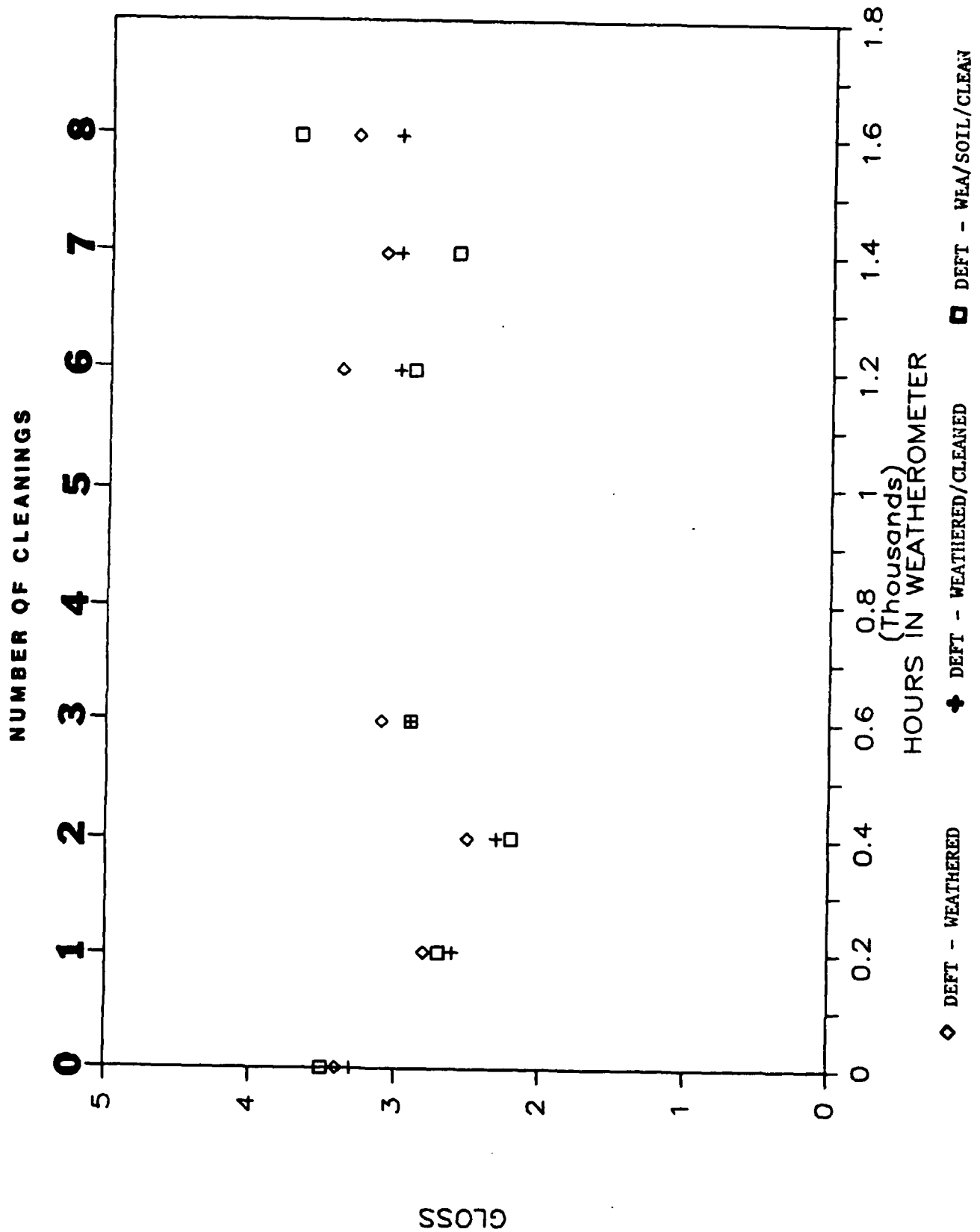


FIGURE 13. GLOSS VERSUS HOUR IN WEATHEROMETER FOR DEFT WEATHERED, WEATHERED/CLEANED, AND WEATHERED/SOILED/CLEANED SPECIMENS

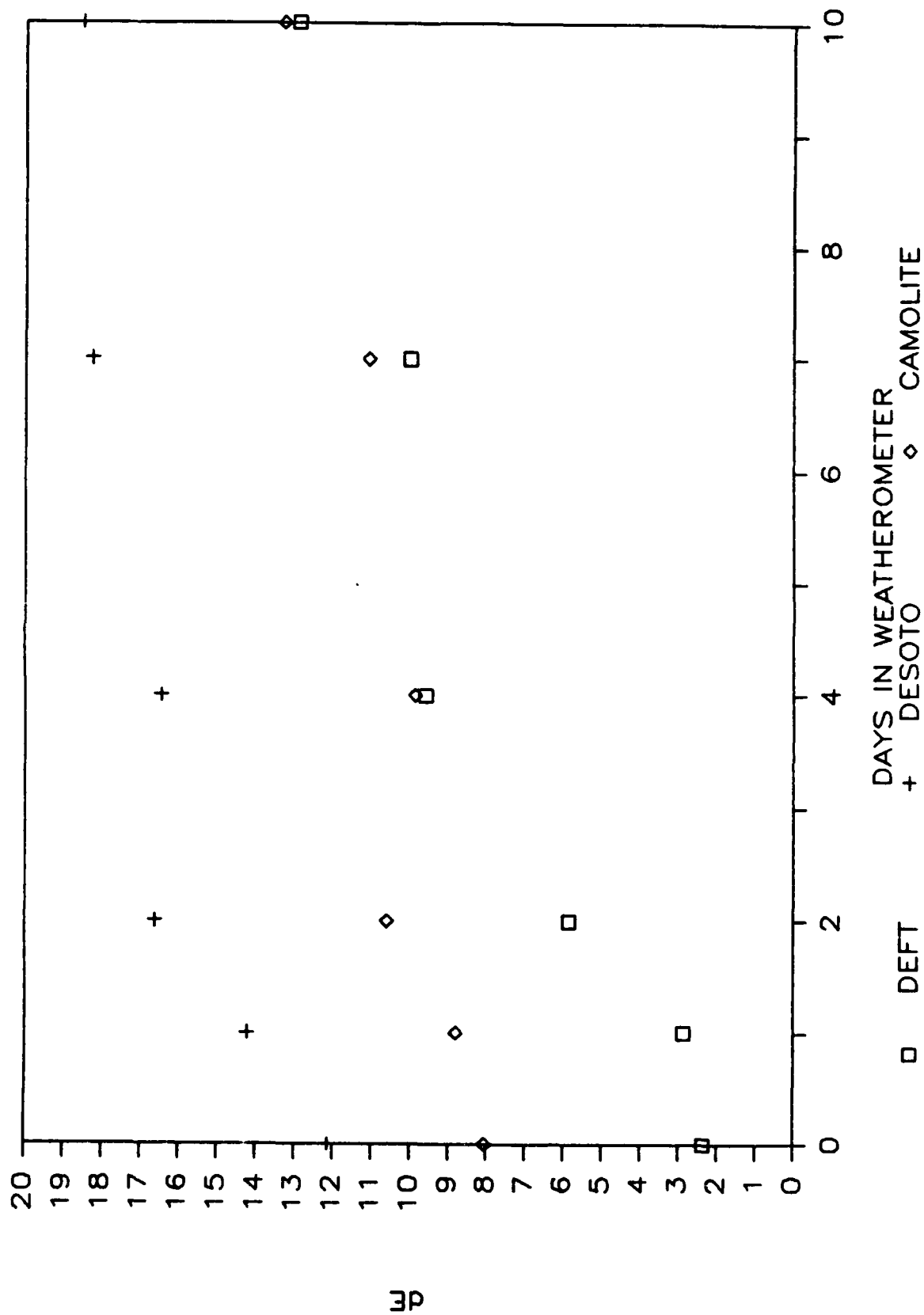


FIGURE 14. COLOR CHANGE, dE, VERSUS DAYS IN WEATHEROMETER FOR SOILED/WEATHERED/CLEANED TOPCOATS

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