PreTreat '93 Conference

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Pretreatment of Plastics

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Pretreatment of Plastics Prior to Painting

Over the last several years the use of plastic surfaces has expanded rapidly. While the automotive industry has certainly lead the way, other industries also make extensive use of polymeric surfaces in the construction of finished products. Many of these parts must be painted in order to fully realize the benefits of plastic surfaces. Painting is done to improve appearance, produce a color match with other parts of the finished product, improve the stability of the plastic surface, or produce a special effect determined by styling or design.

To assure that the painted article meets the performance requirements of the manufacturer or final customer, plastic surfaces undergo some type of pretreatment. The types of soils (Table 1) which the pretreatment removes include: 1) Substrate components at or near the surface which can interfere with paint performance, 2) Processing aids needed in the manufacturing of the plastic article, 3) Soils produced from operations after molding but before painting and, 4) Soils due to handling or storage.

Table 1 - Typical Soils

Internal Mold Releases	Metallic Fatty Acid Salts, Oils,Polymers
External Mold Releases	Waxes, Metallic Fatty Acid Salts, Polyvinyl Alcohols, Vegetable Derivatives
Substrate Components	Plasticizers, Antistats, Lubricants, Flame Retardants, Heat Stabilizers, UV Stabilizers, Fillers, Monomers
Shop Soils	Handling Soils, Lubricants/Oils for Equipment, Marking Soils, Smoke Tar, Dust
Fabricating Soils	Sanding Dust, Aerosols from Air Lines, Flashing Residuals, Lint, Handling Soils

There are three major types of pretreatment processes used to prepare plastic surfaces prior to the application of any organic paint film. These processes are hand wiping, solvent cleaning, and aqueous based power washing.

Hand Wiping

Hand wiping can be done with a variety of solvents or combination of solvents. This type of process is very labor intensive and usually used with low production volumes or in the preparation of prototype parts. Hand wiping can result in large inconsistencies in quality. This is due to a combination of potential human error and the redeposition of soils onto the parts due to contaminated rags used in the hand wiping process. The solvents used in this type of pretreatment can be a large source of air pollution due to VOC. It is estimated that less than 5% of all plastic surfaces pretreated prior to painting use the hand wiping technique. In many situations this process is being replaced by aqueous based processes using a power washer.

Solvent Cleaning

The second type of pretreatment process used for plastics prior to painting is solvent cleaning. The most common method of solvent cleaning is vapor degreasing. Although this technique has been in successful operation for many years at numerous locations, the Federal restrictions on chlorinated solvents are forcing the replacement of this type of process with aqueous procedures. The movement away from vapor degreasing operations to aqueous based processes is also occurring in Japan and Europe.

Aqueous Based Cleaning Processes

The aqueous based pretreatment of plastics prior to painting offers many benefits to industry. These processes operate with relatively low costs, have low environmental impact, are well suited for high production volumes, and have very consistent quality. They are also easy to operate and maintain as demonstrated by numerous current production lines. An industrial power washer usually consists of an overhead or floor conveyer with parts mounted on racks which pass through various spray stages of the process. A typical sequence is shown in Figure 1. Although the same technology can be used in an immersion process, over 90% of all current plastic power wash systems are spray.

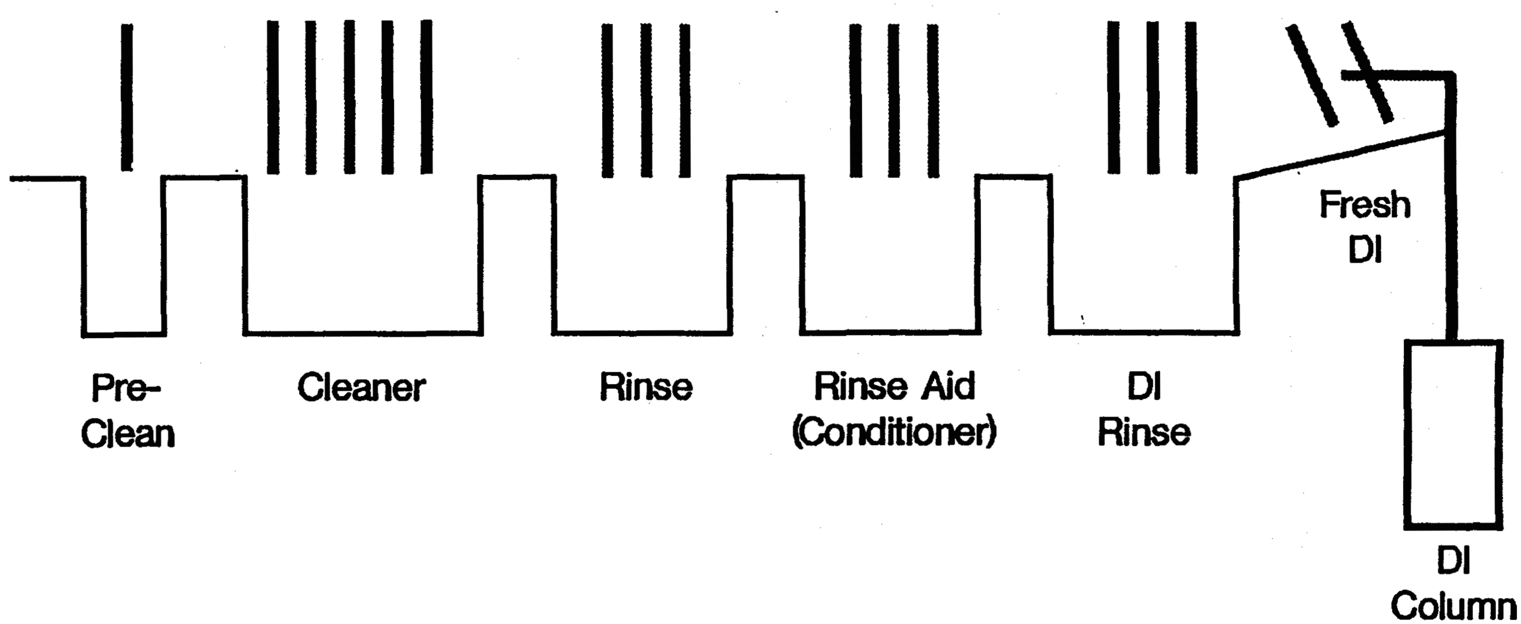
A high quality process is composed of seven separate functions: Precleaning, Cleaning, Rinsing, Conditioner or Rinse Aid, DI Rinsing, Air Blow Off, and Oven Drying.

Preclean

The precleaning step consists of a short exposure, usually between 15 to 30 seconds, of a tap water rinse. This serves to remove gross quantities of soils and decreases the amount of soils going into the main cleaner stage that follows. This can result in increased cleaner bath life in the main cleaning stage. Water for this stage can be supplied from the first rinse after the cleaner resulting in conservation of water. Using the rinse water has the advantage of having water which contains a small amount of cleaner due to the drag in from the previous stage. This residual cleaner will assist in the removal of soils in the preclean stage. In some industrial power wash systems this stage may not have a separate

Figure 1

APPLICATION EQUIPMENT



tank but simply one or two risers of nozzles. The effluent will then flow directly to drain after spraying the surfaces.

Cleaning

The surfaces are next exposed to the main cleaning stage after an appropriate drain zone. This stage utilizes formulated cleaning solutions which are developed to remove specific soils which are encountered with plastic substrates. As mentioned before, soils can include internal mold releases, external mold releases, sanding and finishing dust, handling soils, and other general shop soils. The cleaning stage with spray application is usually 45 to 120 seconds in duration and operated at 20 - 30 PSI fluid pressure. Operating temperature ranges from 120° to 170°F, with cleaners based on older technology operating at the higher end of the range. Cleaners based on newer technology utilize improved surfactants and have excellent detergency at the lower end of the temperature range. Figures 2 and 3 are examples of good and poor cleaning while Figure 4 shows poor paint adhesion due to poor cleaning.

Most cleaners used today are acidic products, with fewer than three percent of the cleaner applications in North America being alkaline. The acidic products clean all typical soils and assure complete rinsing of objectionable residuals. Current acidic cleaners are based on phosphoric acid and operate at a pH of 2.5 - 3.5. While this type of product produces satisfactory results as far as cleaning is concerned, there may be serious drawbacks such as the attack on mild steel equipment and the issue of emitting phosphates into the environment or the need for waste treating prior to discharge to the sewer or local water system. Recently

Figure 2

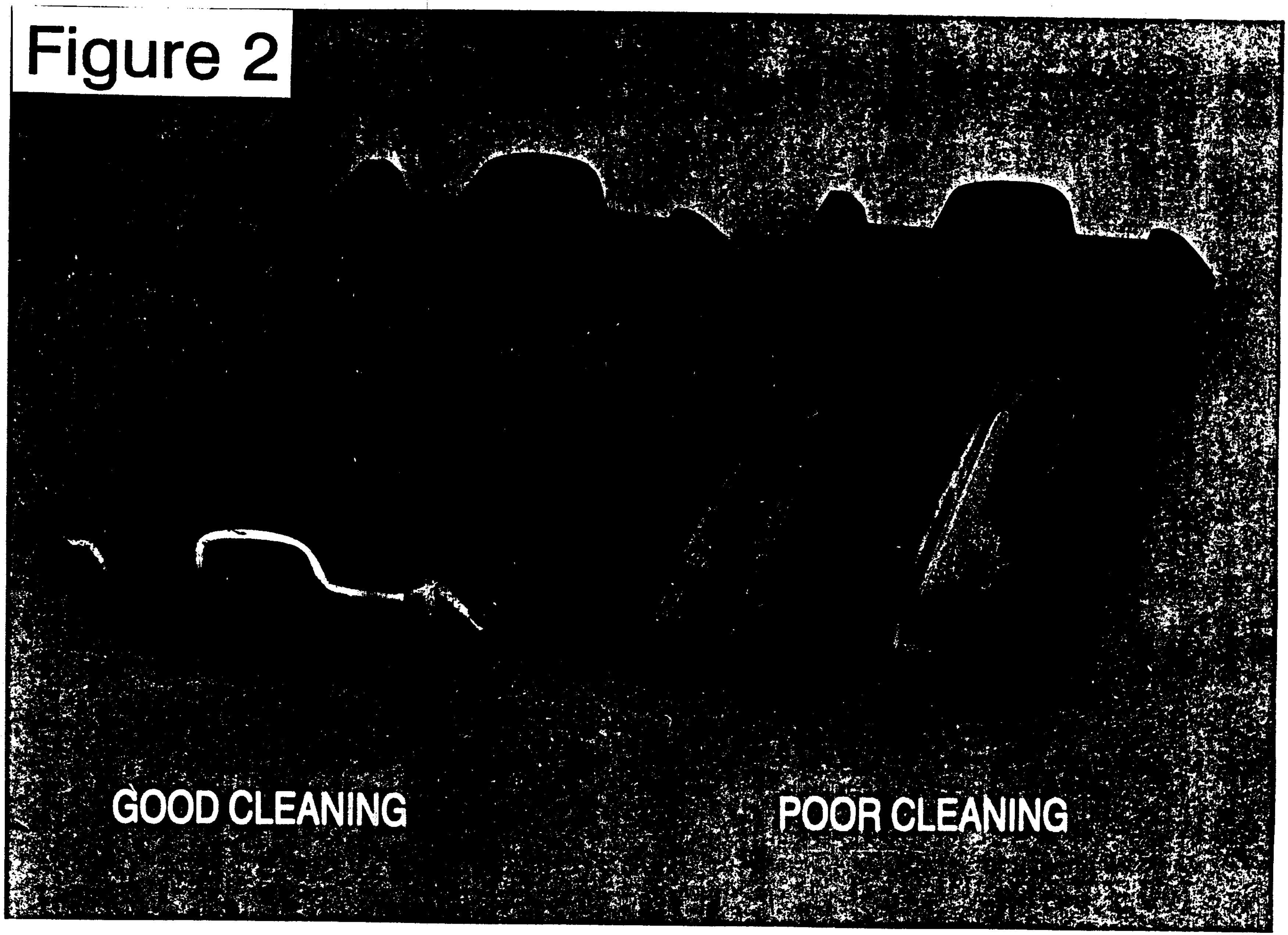


Figure 3

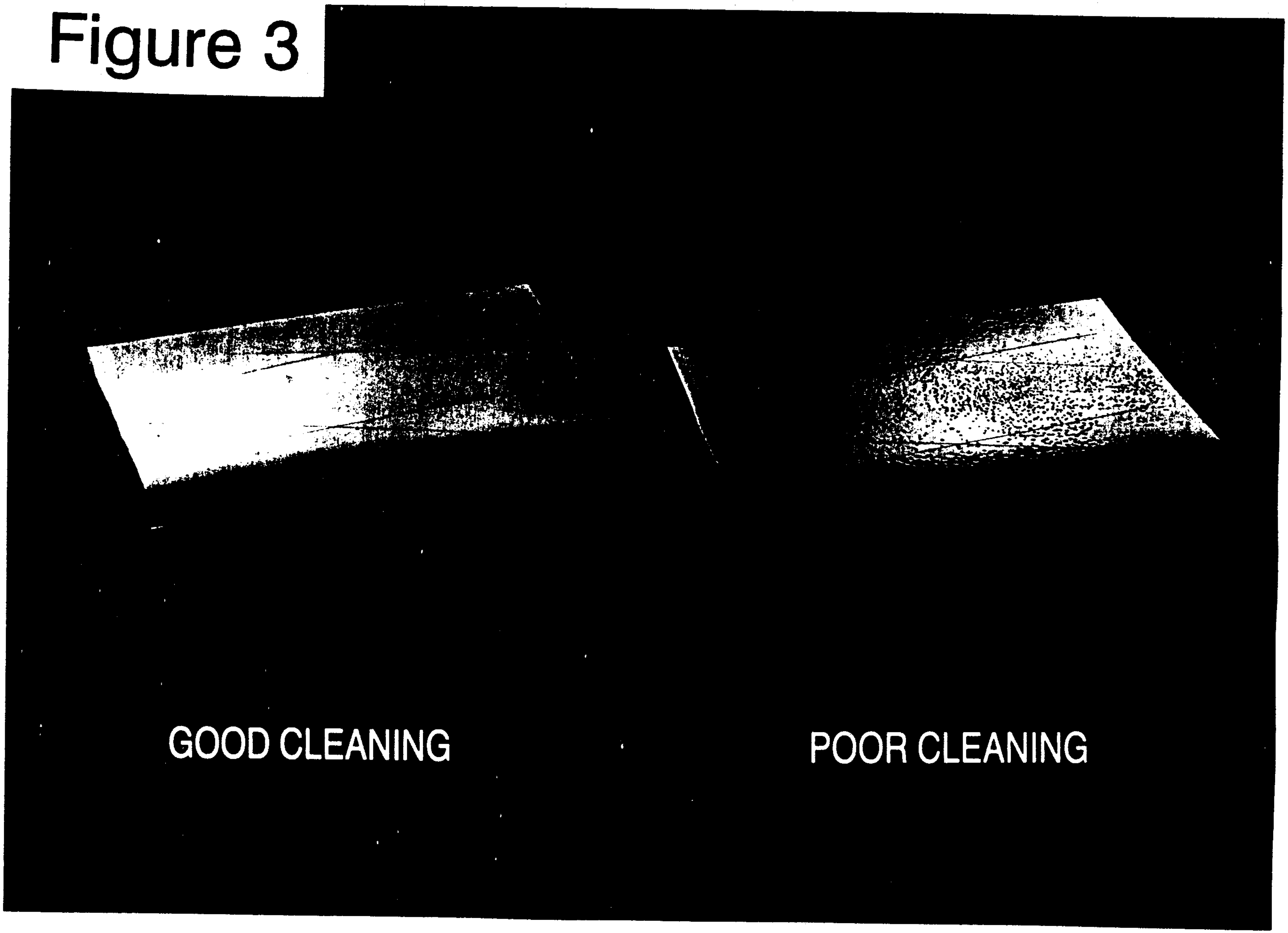
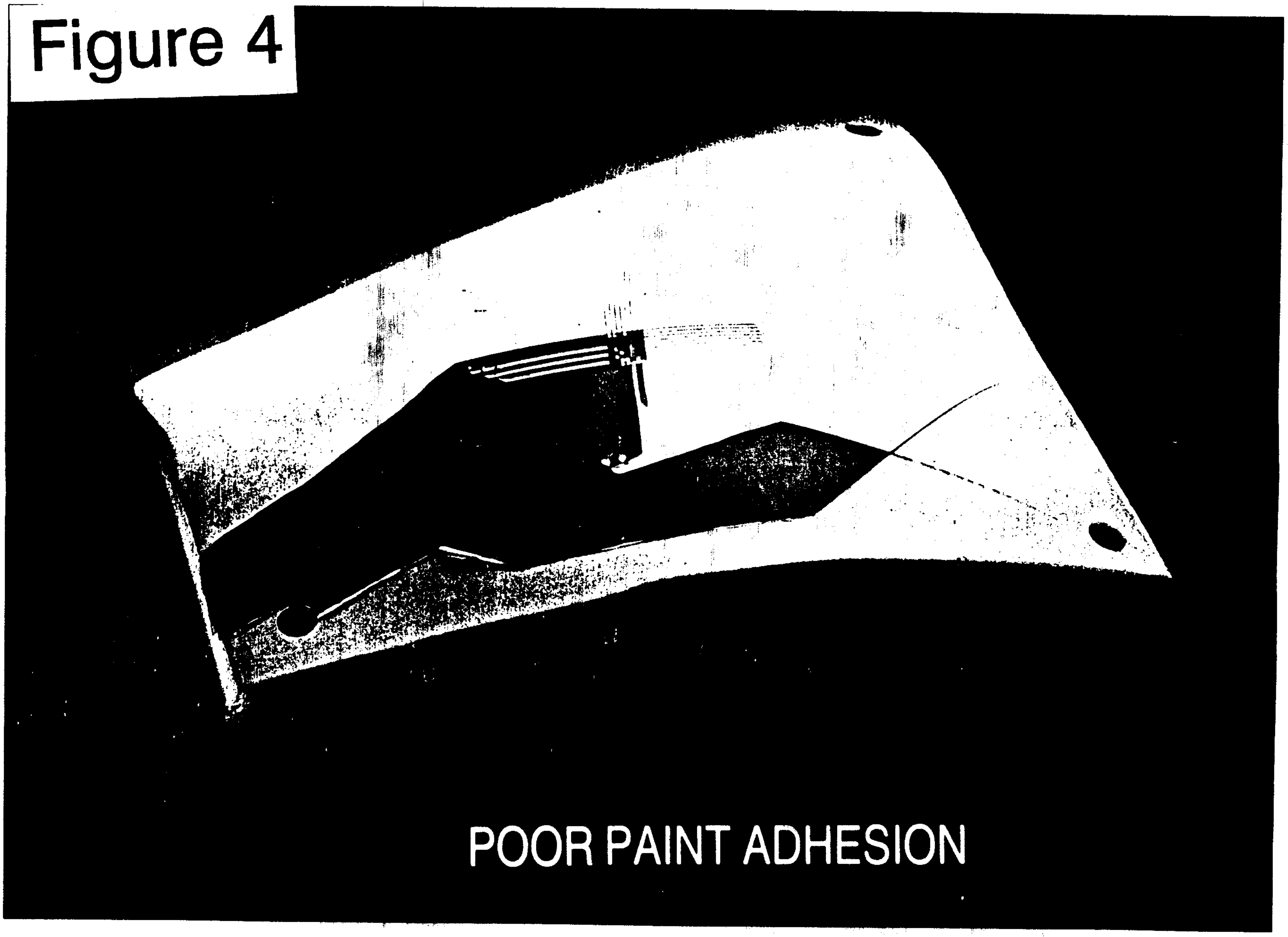


Figure 4



POOR PAINT ADHESION

non-phosphate acidic cleaners have been developed with equal cleaning performance to the previously used phosphate based products but without the environmental concerns and the issue of attack on mild steel. Table 2 shows the features of this new technology.

Table 2 - Non-Phosphate Acidic Cleaner
Excellent Cleaning
Wide-Range Plastic Surfaces
Reduced Waste Disposal
Safe on Mild Steel
Suitable for Existing Equipment

In many plastic painting facilities there is a considerable amount of loose dirt or dust particles on the surfaces to be cleaned. This dust most often comes from sanding or finishing of the plastic parts in preparation for painting. Most cleaners can easily remove this type of particle soil for the plastic surface. As the cleaner is continuously recirculated, the amount of particulate matter present in the cleaning solution will increase to a level where redeposition of the particles on the parts can occur. Even a small amount of particulate matter on the surface can produce paint appearance problems, therefore, a filtration system is recommended for the cleaner stage.

Water Rinse

Next, the surfaces enter a tap water rinse stage. The purpose of this stage is to remove residual cleaner chemicals from the surface and so prepare the surface for the application of the rinse aid/conditioner which follows. It is useful to view rinsing as a process of dilution. Consequently, the fresher the rinse water, the more efficient is the rinse. In order to best maintain a fresh rinse, it is necessary to continuously overflow the tank. The overflow rate should be adjusted so that the contamination level in the rinse stage does not exceed 1 - 3% of the concentration of the cleaner chemical. Overflow rates of 5 - 10 gallons per minute are common for a typical system of 2000 - 5000 gallons capacity. As with the cleaner stage, a filtration system is also recommended for this rinse. Typical exposure time for rinsing is thirty seconds with an operating temperature of ambient to 120°F. In some operations two or more rinses are used.

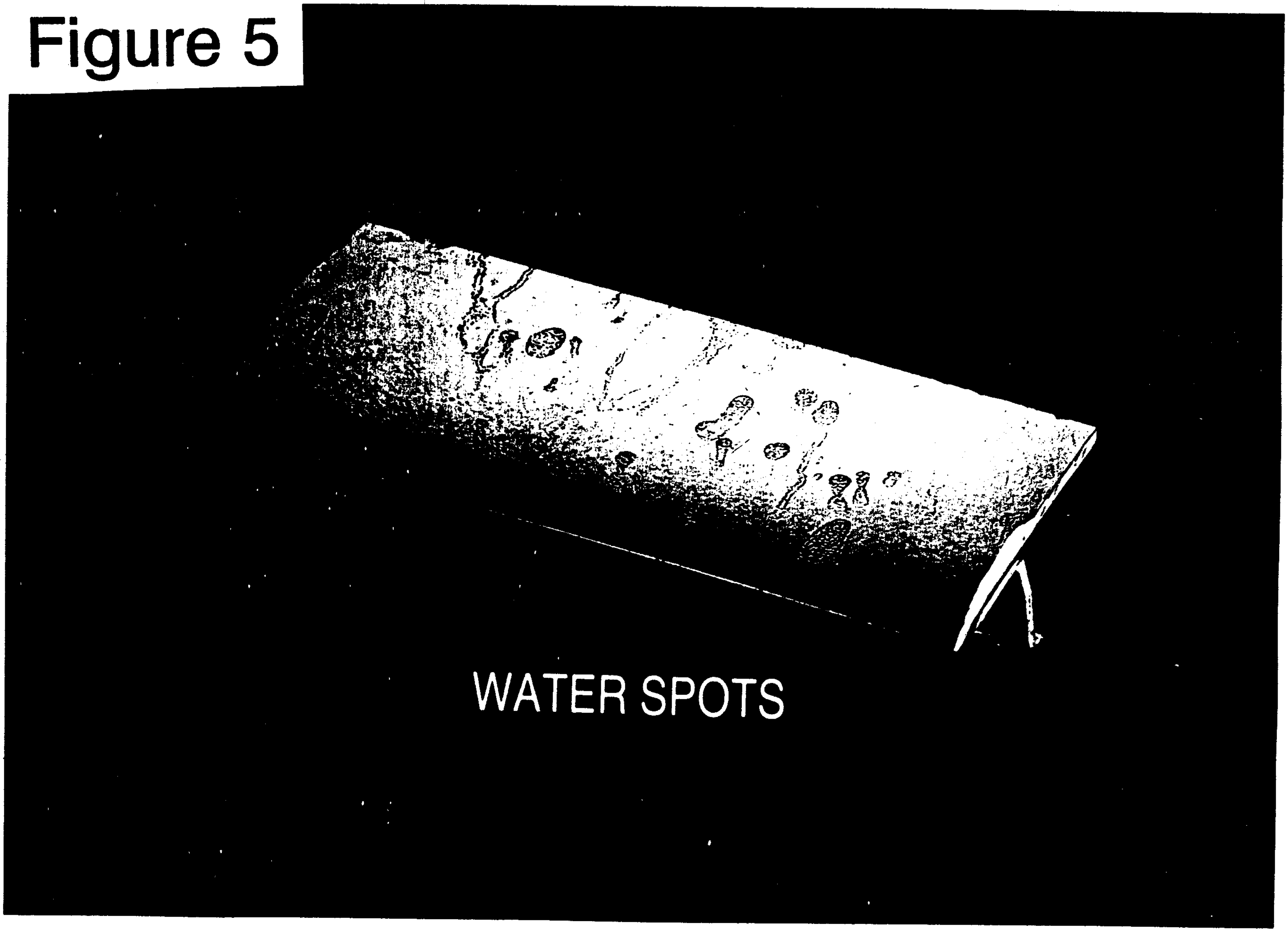
Conditioner

The next stage in many processes is another rinse which frequently contains additives or "conditioners". This conditioner stage is very important when alkaline cleaners are used because, if any alkaline residuals are left on the surface and painted, the paint cure can be affected as well as visual and performance defects produced. With the use of acidic cleaners the technical purpose of this type of conditioner is questionable.

Rinse Aid

In many of today's operations the conditioner chemicals are being replaced with rinse aid products.(1) The function of this step is to assist in rinsing and reduce or eliminate the occurrence of water spots on the parts after drying. Figure 5 shows the poor appearance when water spots are on the surface prior to painting.

Figure 5



Two major types of rinse aid products are currently in use. One is a surfactant type which modifies the surface tension of the water and allows the surface of the plastic parts to be wet with water in an even, break-free sheet. With these water modifying rinse aids, there is no enhanced wetting of the surface in the following rinse stage or stages, and water remaining on the parts will be beaded water droplets. The possibility of water spotting, therefore, still exists. In some operations this type of rinse aid is added to the recirculated DI water rinse, or even the fresh DI water step in an attempt to produce a water break-free sheet to minimize the occurrence of water spotting. By using this technique surfactant residuals will be left on the surface and will not be evenly distributed. High concentration areas such as drip edges risk cosmetic and performance failures.

A second type of rinse aid technology, a surface-modifying polymeric material, is currently in use. With this technology, when the rinse aid solution comes in contact with the plastic surface, a reaction occurs which changes the normal hydrophobic plastic surface into a hydrophilic surface. Figure 6 shows the effect of this product. The advantage of this type of rinse aid is that the hydrophilic effect will withstand rinsing. Therefore, after rinsing, only a thin uniform layer of this material remains. Any excess not reacted is easily rinsed away. Figure 7 shows a possible mechanism for this type of rinse aid. The amount of the material which remains on the surface is extremely low - less than one milligram per square foot and less than 50 angstroms in thickness. This type of rinse aid material maintains the

Figure 6

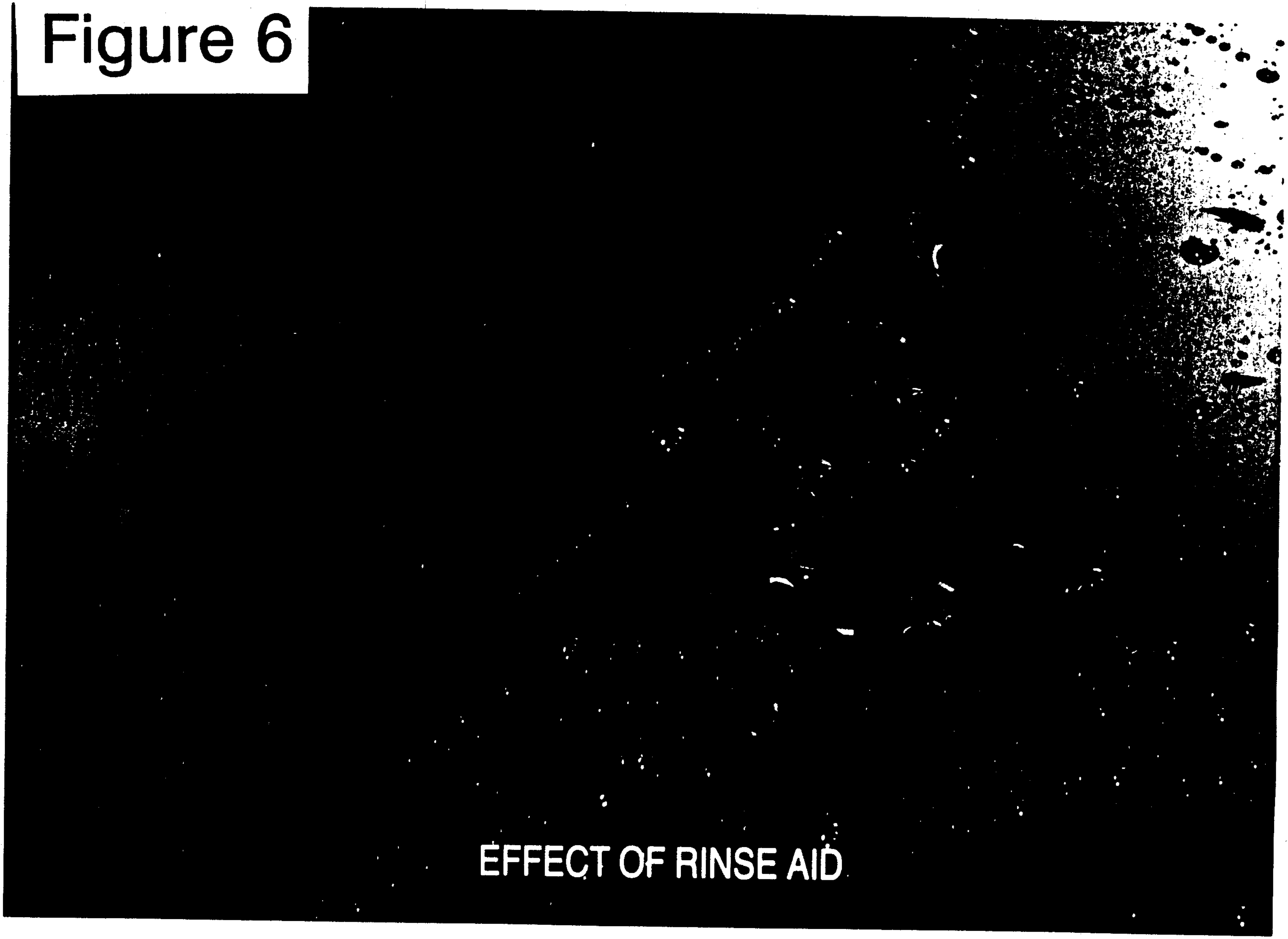
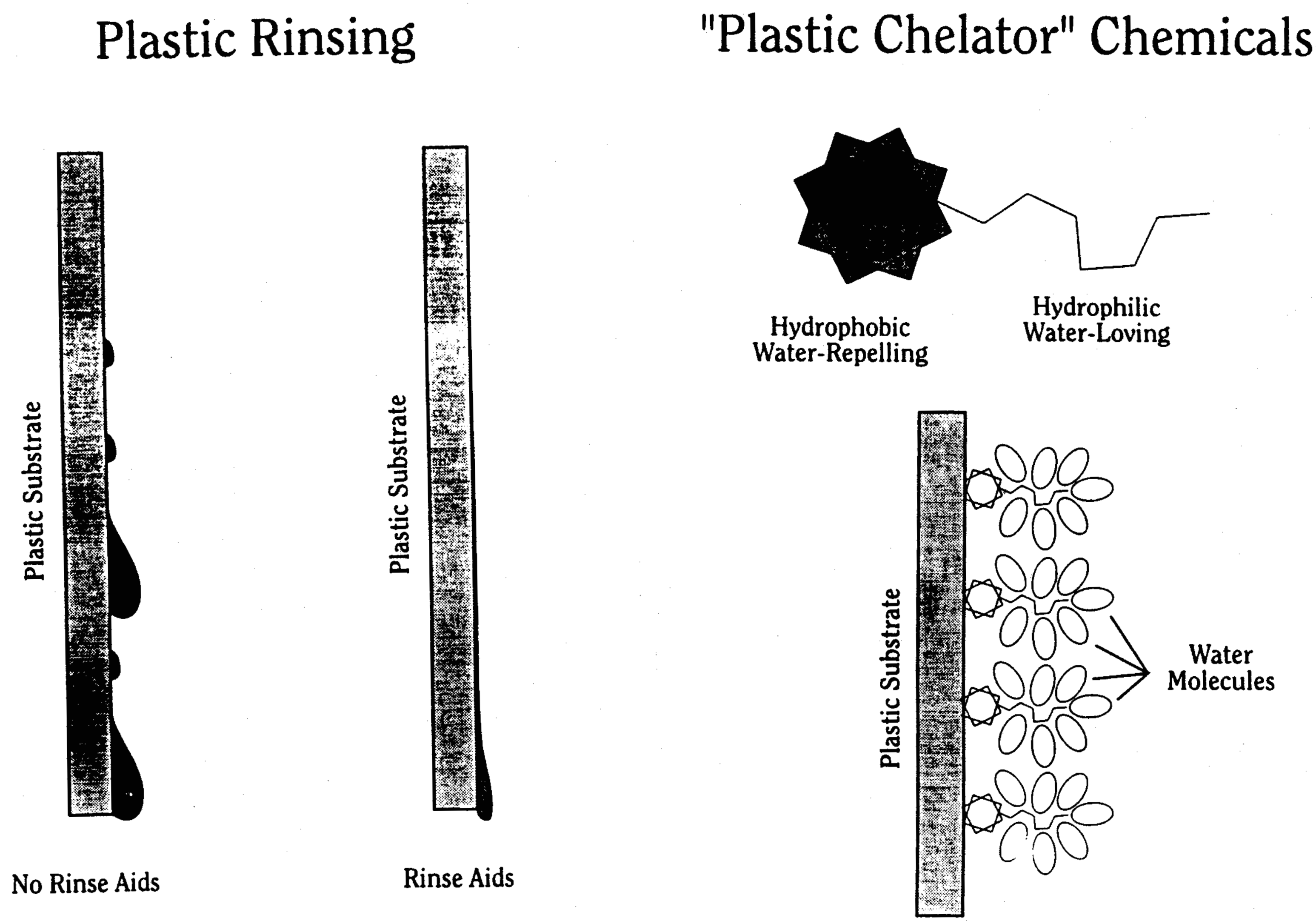


Figure 7


Plastic Rinsing
"Plastic Chelator" Chemicals
Plastic Substrate
Plastic Substrate
No Rinse Aids
Rinse Aids
Hydrophobic
Water-Repelling
Hydrophilic
Water-Loving
Plastic Substrate
Water
Molecules

hydrophilic surface throughout the final rinses. This minimizes or eliminates the formation of water droplets and water spots.

Paint technologists are always concerned that if a layer of any material is left on the surface prior to painting that the paint performance will be affected. Reactive rinse aids have been production proven with over four years of experience with major automotive parts suppliers. There has also been extensive accelerated testing, including Florida outdoor exposure of both production pieces as well as approval panels. All testing and experience have shown excellent performance with a wide variety of plastics and paint systems.

With certain plastic substrates which have extremely low surface energies such as some TPO's, the reactive rinse aids do not lower the contact angle sufficiently to produce a water break-free surface. Developmental activities are underway to improve the technology so that it is suitable for all plastics.

Deionized Water Rinse

The plastic surfaces then move further through the washer and are rinsed with deionized water. The purpose of this rinse stage is to assure that all solids from previous treatment stages are rinsed away. DI rinsing procedure is usually done in two steps - a recirculated step - 20 to 40 seconds - and the fresh step - 2 to 3 risers. The fresh step cascades into the recirculated step (Figure 1). The fresh DI should have a conductivity of 5-15 micromhos while the recirculated DI water should be between 50-100 micromhos to assure proper rinsing. The recirculated stage should be overflowed with enough quantity of fresh DI water to maintain a low conductivity and minimize salt deposits or water spots.

Large quantities of DI water may be required to produce good rinsing with minimum occurrence of water spots. In some cases, large volumes of excellent quality water will still leave water spots. This is due to the hydrophobic plastic surface where water beading can lead to inefficient rinsing. When a surface modifying rinse aid is used, the volume of DI water needed for efficient rinsing can be reduced. The reduction is possible because it requires far less water to replace or remove the thin film of water produced on the hydrophilic plastic surface and the fact that droplets are joined rather than isolated. The amount of reduction may vary according to the substrate processed, application equipment, part configuration, and other production factors.

The fresh DI water feed to the washer and the recirculated DI step should have fine filters on them. The filters will remove fine particulate matter and keep the plastic surfaces free of any troublesome particles as they proceed to the air blow off and dry off oven prior to painting.

Air Blow Off

Following the DI water rinse step is the air blow off. This step is usually needed to assure that excess water on the parts or hangers is physically removed. This step ensures the removal of any excessive water on the parts so that the dry off oven can dry the parts prior to the painting operation.

The air used in this step must be properly filtered and cleaned so that no accidental part recontamination occurs. A desiccant, fine micron particle filtration system is recommended.

Deionizing air can be used to eliminate any static electric charge build up. If a static charge exists, dust and other airborne particulate matter can easily be attracted and attached to the plastic surfaces and cause paint appearance problems.

When a surface modifying rinse aid is used, the amount of air blow off can usually be reduced due to the thin uniform film of water present on the surface. In some particular locations, the air blow off may even be eliminated without any detrimental effects. Lower air blow off volumes, in addition to saving costs, can improve overall quality of the final painted plastic surface due to less turbulence and, consequently, less chance of airborne particles and water droplets being blown onto the parts.

Dry Off Oven

After power washing, the parts must be dried prior to painting. It must be recognized that internal components of certain plastics such as RIM and SMC can migrate to the surface during the dry off step. These materials on the surface can dramatically affect paint performance or appearance. The lowest workable dry off oven temperature should be used. Surface modifying rinse aids can assist in lowering the amount of heat necessary to dry the parts.

Acceptable dry off oven temperatures and times are extremely substrate dependent. Some plastics show thermal migration problems at temperatures as low as 125°F while others can be dried at temperatures over 300°F without difficulty. Experience has shown that even the same plastic substrate produced by different suppliers may have different threshold temperatures at which thermal migration begins. The presence of deleterious contaminants from thermal migration are easily seen when a thin coat of paint is sprayed on the surface. This is qualitative observation. Affected areas show paint pulling away or dewetting caused by differences in surface energy between clean and soiled regions. The effect can be measured quantitatively by contact angles on cleaned parts before and after the dry off. This technique is described later.

The optimum dry off oven temperature of a particular line should be established experimentally with assistance from suppliers. The part temperature should be monitored periodically to assure that the minimum threshold temperature is not exceeded.

Evaluation of Cleanliness of Plastic Surfaces

Since the earliest use of painted plastic surfaces, there has been a real need for a test to determine the cleanliness of the surface prior to painting. The most widely used method has been to subject the parts to the entire cleaning and painting operation and then test them for adhesion or other performance tests. While this is obviously useful information, the results are ambiguous if there is a failure. Paint adhesion loss can be caused by substrate raw material difficulties, molding inconsistencies, poor cleaning, re-soiling of parts, or numerous paint issues.

Research activities have shown that the measurement of contact angles or surface energies has promise as a test for determining the effectiveness of cleaning of plastics. Figure 8 shows the concepts of measuring the advancing and receding contact angles. When these measurements are made on a plastic surface before and after cleaning, an estimate of the surface cleanliness can be made. Figure 9 charts an example of contact angle measurement on a typical automotive plastic.

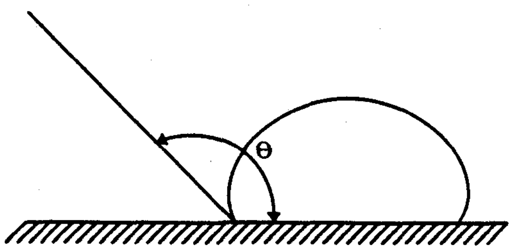
This technique has several drawbacks. In some cases the variation of the measured contact angle of the uncleaned surface from location to location, is larger than the average reduction in the contact angle by cleaning. Therefore, the magnitude of contact angle reduction at several surface points after cleaning can be "noisy". To gather meaningful data, the same point on the surface should be used to measure the contact angles before and after cleaning. This reveals the change in contact angle due to cleaning while minimizing the effect of surface variation. Contact angle measurement appears to be a useful diagnostic tool for determining the relative effectiveness of various cleaners and/or cleaning conditions. Additional data and experience must be obtained before this tool can be used to reliably predict paint performance of a painted plastic surface.

Automatic Control Equipment

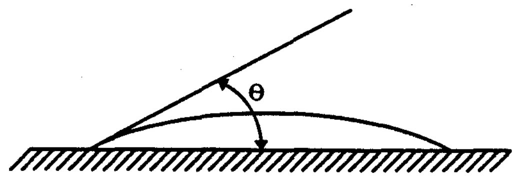
Once a particular process has been optimized, automatic control equipment can be used to maintain the concentrations of the chemicals at the desired levels. Complete sense and feed back

Figure 8

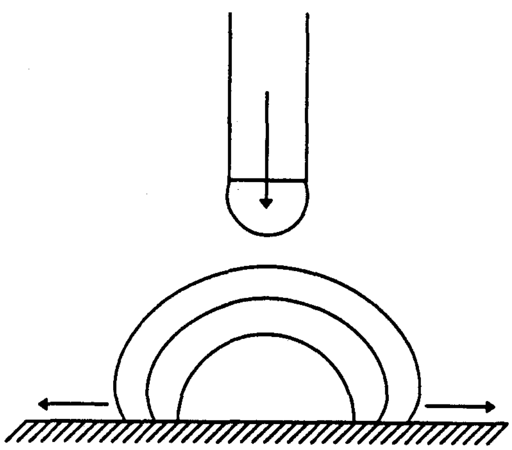
Measurement of Contact Angles



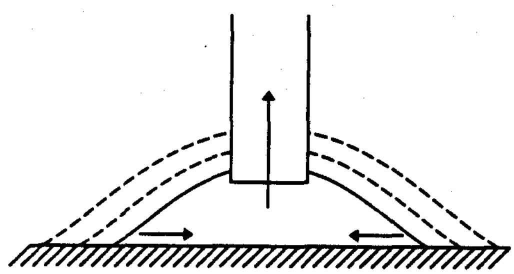
High Contact Angle
Hydrophobic



Low Contact Angle
Hydrophillic

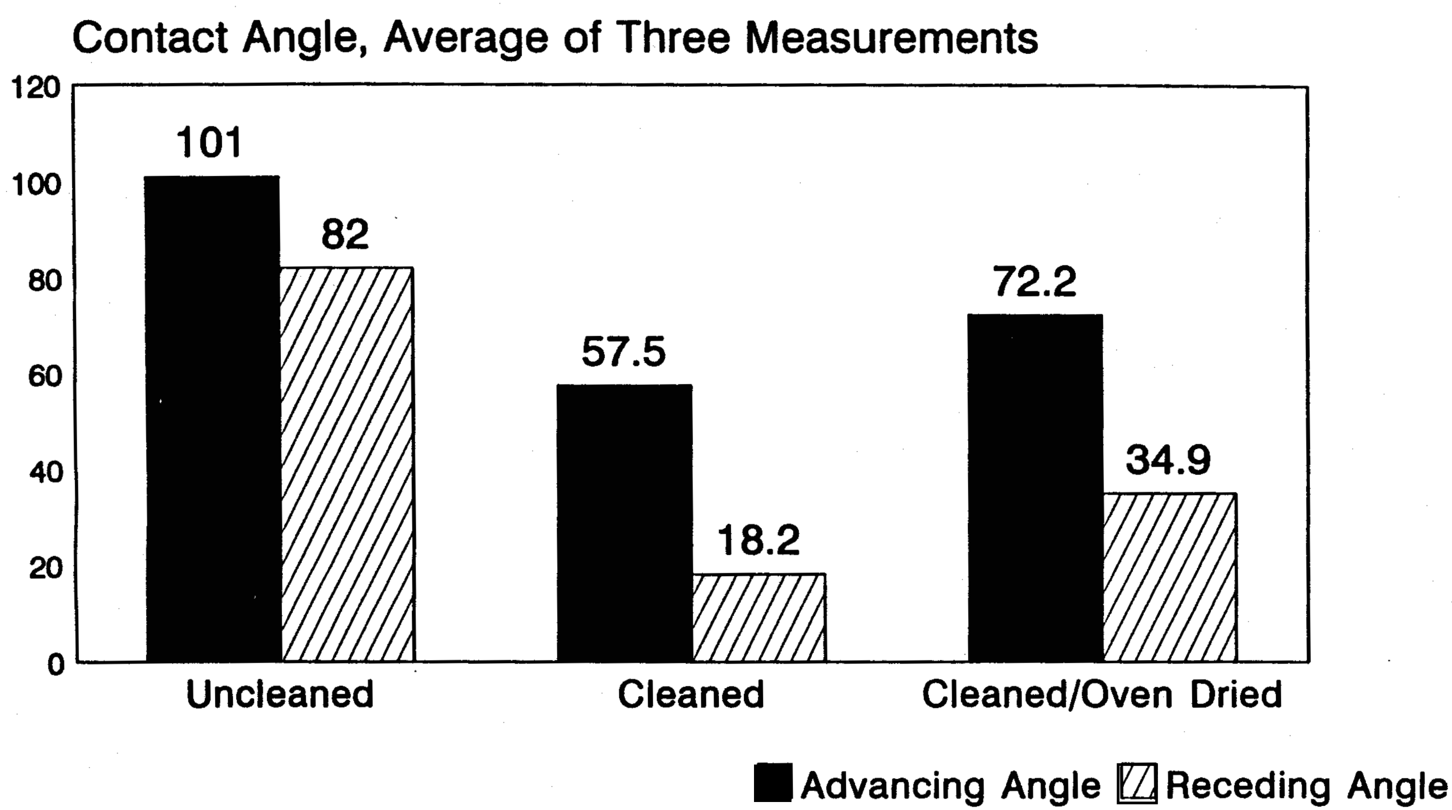


Advancing Contact Angle
Solution added to droplet measures largest possible angle.



Receding Contact Angle
Solution withdrawn from droplet measures smallest possible angle.

Figure 9 - Cleaning Effectiveness
Contact Angle Measurement



Substrate: RIM Urethane
Spray Cleaning-Acidic,Rinse,Rinse Aid,DI Rinse
Dry Off Oven-190 F, 10 Minutes

systems which are available control the cleaning and rinsing chemicals within narrow ranges. Consistency of concentration assures reliable cleaning with reduced operator intervention. Advanced control systems are available to maintain and record solution levels, process temperatures, spray pressures, water usage, chemical consumption, dry off oven temperature, effluent volumes, and even many parameters of the painting operations. An additional benefit of control systems is that SPC data can easily be generated. Some systems have SPC capability built in while less expensive ones have data storage capability. The data can then be down loaded into a PC with a SPC program to create control charts.

Summary

Painted plastic surfaces are becoming more widely used. For maximum performance of any painted plastic part, a high quality cleaning process must be used. Multi-stage aqueous power washing processes have proved to be extremely effective in cleaning plastic surfaces prior to painting. Care must be taken to assure that each step is continuously operated and maintained at the proven parameters which assure acceptable pretreatment. The air blow off and dry off oven steps must also be closely controlled to maintain consistent quality.

Acknowledgements

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Reference

1 "Rinse Aid Technology for Improved Rinsing of Plastic Surfaces", Theodore D. Held, Society of Manufacturing Engineers, 1992, EM92 182