Clifford K. Schoff

Dr. Schoff currently leads the Automotive Physical Chemistry Group at PPG Industries, Inc., Allison Park, PA. He joined the company in 1974 and previously held Post-Doctoral appointments at Glasgow University and at Princeton. He received B.S. and M.S. Degrees in Chemistry from the University of Idaho and a Ph.D. in Polymer Chemistry from the University of St. Andrews in Scotland. However, his main training in problem solving came from his experiences as a Peace Corps Volunteer teacher and coach in Nigeria after he received his Masters Degree.

Dr. Schoff began his coatings career in the Physical Chemistry Group at PPG's Allison Park Research Center near Pittsburgh where he was trained by industry stalwarts Charles Hansen and Percy Pierce. He worked on a wide range of problems in all product areas and did research on paint rheology, mechanical properties of solid coatings, surface defects, and electrodeposition-substrate interactions. He also taught coatings technology to colleagues in numerous countries. In 1991, he moved to the Automotive Research Department. His current responsibilities as head of the Automotive Physical Chemistry Group include problem solving for PPG's worldwide automotive coatings business.

Dr. Schoff has authored over 30 publications, including the monographs, "Rheology," and (with Percy Pierce) "Coatings Film Defects," published as part of the FSCT Series on Coatings Technology. He has given over 70 presentations in the U.S. and overseas. He pioneered several techniques, including videotaped hot plate bakes for recreation of surface defects and the use of rolling ball viscosity measurements to characterize film and defect formation behavior of automotive coatings. He has contributed to product successes in high solids, waterborne, electrodeposition, and powder coatings, as well as to the understanding and solving of many problems, particularly surface and dirt defects at customers' plants.

Dr. Schoff is an active member of the Pittsburgh Society where he worked his way through the chairs and was President in 1985. A member of the Editorial Review Board of the JOURNAL OF COATINGS TECHNOLOGY, he is Chair of the Roon Awards Committee. Dr. Schoff was the Program Committee Chair for the 1993 FSCT Annual Meeting. He has served on other Federation committees, including the Professional Development Committee and the Mattiello Memorial Lecture Committee, of which he served as Chair in 1995.

Also active in ASTM Committee D-1 on Paints and Related Materials, he recently relinquished the Chairmanship of Subcommittee D01.24 on physical properties of liquid paints which he held for 19 years. Dr. Schoff received the William T. Pearce Award for outstanding contributions to the science of testing paint and materials in 1987 and the ASTM Order of Merit in 1992. In 1996, he was elected to Honorary Membership of Committee D-1 and was made a Fellow of ASTM.

In addition, Dr. Schoff is a member of the American Chemical Society, Society of Rheology, Society of Automotive Engineers, and Sigma Pi Sigma (Physics Honorary).

He has been a lecturer at short courses for Kent State and North Dakota State Universities, University of Wisconsin Milwaukee, and for the Federation. Dr. Schoff has given lectures at a number of universities in the U.S. and abroad.

1998 Mattiello Memorial Lecture

Surface Defects: Diagnosis and Cure

Clifford K.Schoff—PPG Industries, Inc.*

Surface defects are as old as paint itself and have plagued generations of paint technologists. Some people think that we should have cleaned up the defects and gotten rid of them years ago, yet they are more common than ever. Why do defects occur so often? Why are coatings so different from the materials they coat? Why is it so difficult to solve defect problems? What can we do about them? This paper attempts to answer these and other questions. It addresses a number of defects and their causes, including craters and other surface tension related defects, dirt (the most common defect of all), popping, and flow problems. It also reviews techniques for defect identification and root cause analysis and discusses countermeasures. Examples and case histories are used to illustrate defects and methods of attack to characterize and cure them. The communication and organizational difficulties that often compound defect problems rather than help solve them also are considered.

INTRODUCTION

When I was first asked to give the 1998 Mattiello Lecture, I thought of a number of different topics, including mechanical properties of coatings, cure and cure characterization, and problem solving. I felt that Percy Pierce and I had covered surface defects several years ago with our Federation booklet on the subject.[1] However, discussions with colleagues and continual encounters with surface defects made me realize that defect problems have not gone away or even been reduced. In fact, they are worse than ever. They still hurt both appearance and protection. So, I decided that I would revisit this area, particularly since plant work in the last few years has enabled me to look at defects from a different viewpoint.

We have had customers tell us that "by now, the coatings industry should have been able to design paints that do not give defects." When you think about it, that means paint that resists all contaminants, can be applied under any and all conditions, etc. This is a tall order and an unrealistic one. However, there is no question that we should be able to do a better job of designing and manufacturing paints that are more robust, do have wider application windows, and do come closer to keeping customers happy. If we do not accomplish this, we are going to wake up some morning to find that other technologies, not paint, are being used to provide surface appearance and protection.

Let us look at some of the reasons why there is a gap between customer expectations and what we deliver today. What separates coatings from other materials used in automobiles, washing machines, furniture, and other objects and structures that we paint? For one thing, coatings usually are applied as liquids (paints), yet end up as solids (coatings). Paints must wet the surface of whatever they are applied to and stay there. They must flow and level, but not flow too much. Then, they must be cured, i.e., air dried and/or baked, to be changed into tough, adhering solid films. This description certainly does not fit materials such as steel, wood, or plastic. Other things that set coatings apart is that they are thin, are complex mixtures which become composites on drying and curing, have large surface areas, usually come in layers, and have large and multiple interfaces. Last, but not least, coatings must look good. In many applications, the first three requirements are appearance, appearance, and appearance.

What do these unique properties of coatings give us?

1) Decoration and protection with incredibly small amounts of material!

2) Many problems/many defects!

Presented at the 76th Annual Meeting of the Federation of Societies for Coatings Technology, on October 14, 1998, in New Orleans, LA.

*4325 Rosanna Dr., P.O. Box 9, Allison Park, PA 15101.

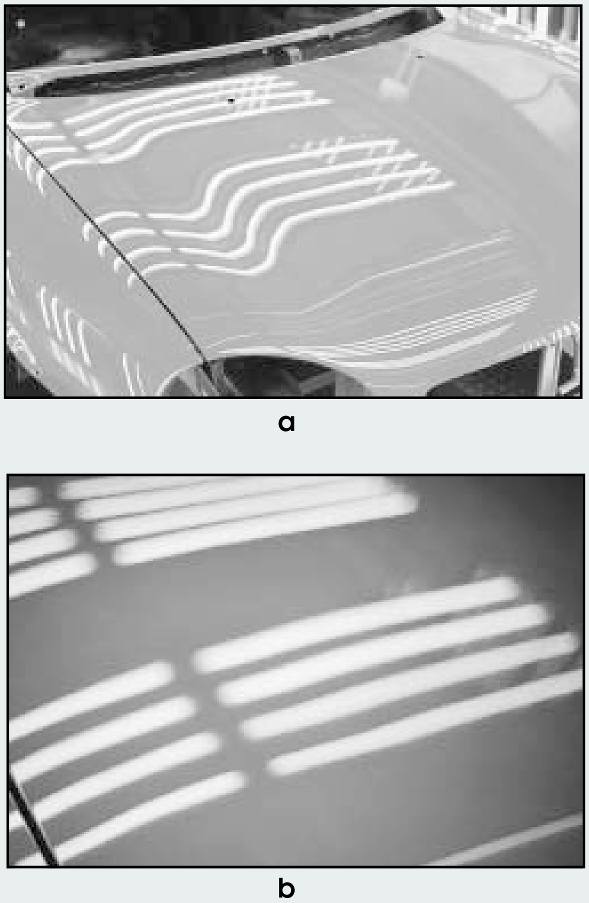


Figure 1—Hood of a car body at the end of the paint line in an auto factory. Bright lights and their reflections are used to evaluate the appearance and locate any defects: (a) General view of the hood. Note paper markers on left hand side showing position of defects (dirt or craters). (b) Closeup of the hood with light reflection showing degree of orange peel.

Most coatings are applied in liquid form and are liquid until they are cured. They must be capable of being transferred from a container to a surface by spraying, rolling, brushing or some other application technique. Because they are liquids, they are dirt catchers and they flow (often too much or too little). Because they are mixtures, they often are heterogeneous and some regions may be rich in one component or another. For good appearance and adhesion, the paint must wet the substrate on application, but it may have difficulty doing so or it may dewet after it has been applied. When a solid film forms, liquids and gases may be trapped, components may come to the surface (or not). Layers may or may not adhere well to each other or to the substrate. The paint technologist must design a paint formula very carefully, then test and fine tune it to avoid these problems. Many properties must be controlled in order for the paint to work at all, much less work well. *Figures* 1a and b show the hood of an auto body at the end of the paint line in the factory. The coatings that comprise the finish on this vehicle have excellent properties, but the surface could be smoother, i.e., could have less orange peel (note the reflection of lights). It is a good finish, but it could be better. If there are 20 requirements, it probably meets 19 of them.

Coatings are not chunks of something like a steel sheet or plate or a wooden board or a plastic bumper. The latter materials usually are homogeneous, have relatively few requirements to meet, and can be designed or treated to avoid most of the potential problems (but not all of them). Although coatings are different, occasionally they can be made to operate more like other materials. For example, it is possible to apply a coating as a sheet, like a tape,[2] or lay it on and shrink it into place like shrink-wrap. However, there have been many problems, both technical and organizational, and applications are limited.

Not only are coatings unique in their properties, they are unique in requiring a tremendous diversity of physical and chemical sciences (polymer chemistry, colloid science, surface physics, fluid mechanics, dispersion technology, etc.) to understand and design them, and to solve problems with them. No other industry demands such a breadth of knowledge from its scientists and technologists. No other technology area is so complex.

This is not to say that we can excuse problems and defects to our customers by saying "well, coatings are just different," but it is true, they are different! After spending time in the field and seeing how many things can go wrong with application equipment, ventilation, ovens, filtration, etc., as well as the paint, I am amazed that there are as few defects as there are. Let us consider some of these defects. I will not cover all the possible defects by any means, but will discuss a few of those that have given me trouble in recent years. See references 1, and 3-9 for additional information.

DEFECTS

Cratering and Other Surface Tension Related Defects

Let us start with the nastiest, most frustrating defect of all, craters. They are one of the most common defects, yet probably are the most difficult problem to solve. Analysis of craters by even very powerful analytical instruments often yields nothing more than the fact that there is paint in the middle. The crater causing material evaporated in the oven or dissolved back into the paint. When a contaminant is identified, we still must find out where it came from.

What exactly is a crater? A crater is a depression in the coating. It occurs when there is a low surface tension contaminant, on, in, or under the paint. The paint flows away from the low surface tension area, leaving a circular defect as shown in *Figures* 2-4. The surrounding paint usually does not move, so the flowing paint runs into the former, causing a slightly raised rim to form (see diagram in *Figure* 5). There are many different sizes and shapes of craters. When the contaminant is on the surface or there is flow back into the crater area (especially in the oven), the result is a shallow crater, a dimple such as the far right hand crater in *Figure* 4. One type of crater is called a fish eye because of its appearance which, not surprisingly, resembles an eye with a raised area in the center (*Figure* 6). When viewed under a microscope, some craters turn out to be constellations of many tiny craters or irregular small dewetted areas (*Figure* 7). Other craters are small pinholes which are difficult to distinguish from pops or gassing.

Cratering may be due to surface tension gradients on the surface of the wet paint or it may be a form of dewetting or not wetting to begin with. Wetting is the process by which a liquid comes into intimate contact with a surface. We think that application processes force the paint to initially cover the substrate, but that may not involve true wetting. Certainly, dewetting or pulling back can occur over regions of low surface tension and can result in defects such as craters. Contaminants that can cause cratering include hydrocarbon and fluorocarbon oils and lubricants, silicones, plasticizers, resin gel particles, oven condensate, dirt, fibers, filter material, overspray, deodorants and other personal care products, poorly dissolved or dispersed additives (especially silicones), and contaminated raw materials.

Dewetting and lack of wetting cause other defects besides craters. Dewetting is responsible for paint crawling away from edges and holes. When a large amount of surfactant is added to a primer to enable it to wet a difficult substrate, the result may be that the topcoat is unable to wet the primer or dewets badly from it. Wiping of a surface with contaminated solvent or wiping with a tack rag dipped in solvent then topcoating can have a similar effect (*Figure* 8). Sometimes dewetting on vertical surfaces leads to sagging because the bead or thick area flows under the force of gravity. Incomplete wetting or dewetting can cause poor knitting (lack of coverage and coalescence) of spray droplets (*Figure* 9).

Dr. William Zisman presented the 1971 Mattiello Lecture on the subject of "Surface Energetics of Wetting, Spreading, and Adhesion."[10] Dr. Zisman developed the concept of the critical surface tension and applied it to various wetting and spreading problems. Twenty-seven years have gone by since then and we still have wetting and dewetting problems! Either we have not listened to Dr. Zisman or the situation is very complicated. I think that both are true.

There are other types of surface tension driven flow, including sinks and bumps ("oven orange peel") where a coating may be very smooth before the oven, but come out all bumpy after the bake, picture framing (*Figure* 10) where a bead builds up along the edge of a panel or part, and Bénard cells (*Figure* 11), surface structures which can affect color and gloss and often involve flocculation as well as surface tension driven convective flow. All of these defects are affected by a combination of surface tension, viscosity behavior, and cure kinetics (which affects the viscosity and how fast the coating sets up).

Dirt

The next defect that I would like to discuss is dirt. Few paint formulators ever think of dirt as one of the

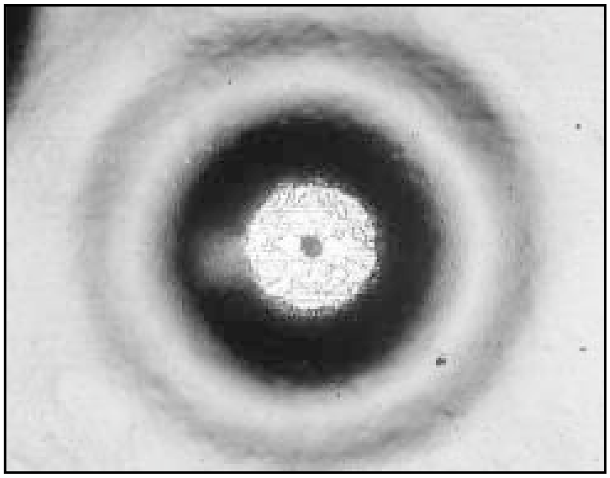


Figure 2—Crater in an automotive basecoat applied directly to metal as part of a series of experiments to identify a contaminant. Photograph taken at 50X.

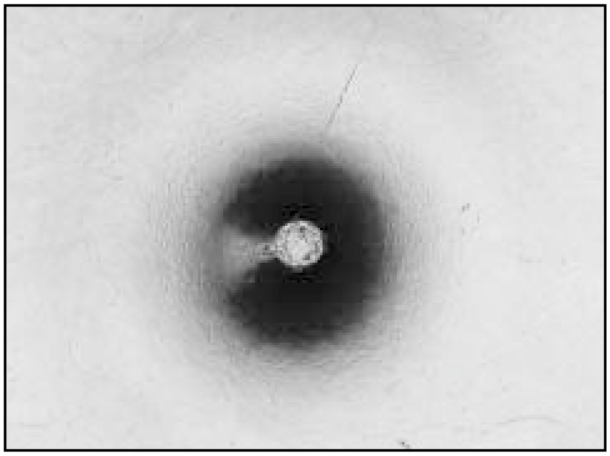


Figure 3—Crater in a topcoat. The hole in the center goes down to the primer. Original photograph at 75X.

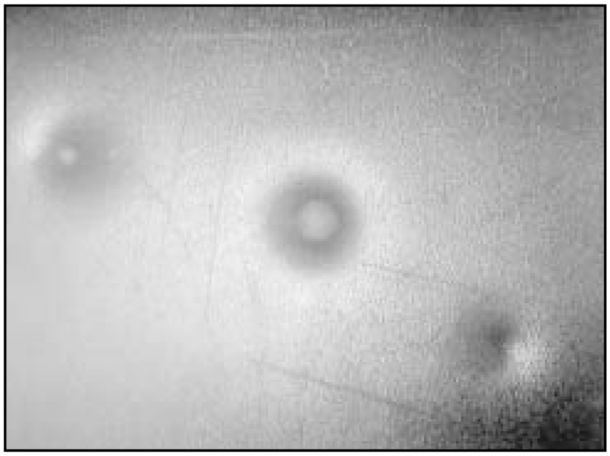


Figure 4—Craters in an automotive primer. These are relatively shallow craters with low or no rims. Photograph taken at 10X.

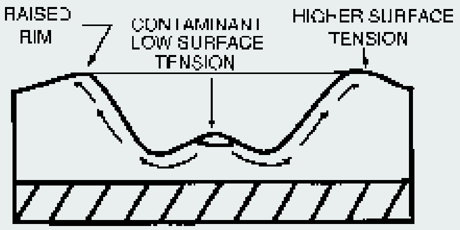


Figure 5—Diagram of a crater showing the flow away from the area of low surface tension (the contaminant) to an area of higher surface tension and the build up of paint to form the rim of the crater.

defects that their paint may suffer. However, service people and customers are continually faced with dirt defects—sometimes dirt in the paint, more often dirt from the customer's facility that falls on that great dirt catcher, wet paint. Dirt probably is the most common defect of all. It usually is seen as dark bumps that disturb the surface appearance. The glossier the surface, the more noticeable the dirt, so dirt is the great enemy of automotive and other glossy coatings. Since paint films are so thin, a dirt particle does not have to be very large to be seen. Even a particle with a diameter less than 100 micrometers may be significant.

There are many kinds of dirt: fibers, sanding dust, overspray, paint chips, rust, weld balls and metal shavings, oven dirt/condensate, gel particles, pigment flocs (seeds), crumbs from workers' lunches, floor dust, etc. Examples are shown in *Figure* 12 with a clump of dirt, most likely from the oven, in an automotive primer and *Figure* 13 with a large fiber in a similar primer. Dirt comes from many sources. Some dirt is inadvertantly supplied by the paint manufacturer (although all batches are filtered carefully), other dirt is generated in the customer's plant (sanding dust, fibers from wipes, tack cloths, clothing, and drips and chips from overhead carriers). Some dirt can come from outside (construction and road dust, locomotive and vehicle exhausts, soot, pollen, particulates from power plants, and other smokestack industries) Other defects may not really be dirt, but look like dirt. The dark spots that occur on silver and light colored metallic coatings usually are assumed to be dirt or pigment seeds, but anything that creates a bump that changes the way that light is reflected and refracted will hurt the appearance and will look like dirt. Examples include basecoat and primer pops, basecoat and primer gun spits and overspray, small metal defects, and air bubbles. The clearcoat often makes the defect more noticeable by acting as a lens over it and magnifying it.

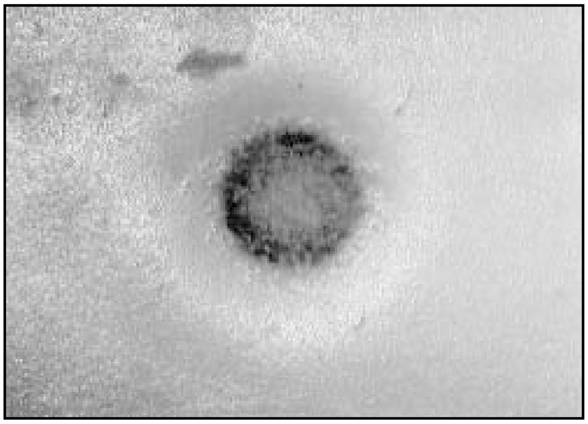


Figure 6—Type of crater called a fish eye. Original photograph at 15X.

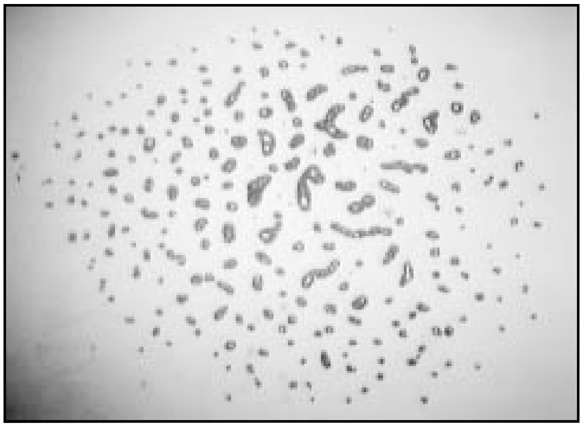


Figure 7—Mass of small craters that looks like one big crater to the eye. Industrial high solids coating. Photograph taken at 6X.

Dirt can cause craters, either by being of sufficiently low surface tension to cause dewetting (such as with some fibers) or by absorbing low surface tension additives or solvent. I have seen a number of dirt craters, and some paints are prone to them, but usually the dirt sits in or on the paint without giving craters. In fact, customers' plants with dirt problems rarely have craters.

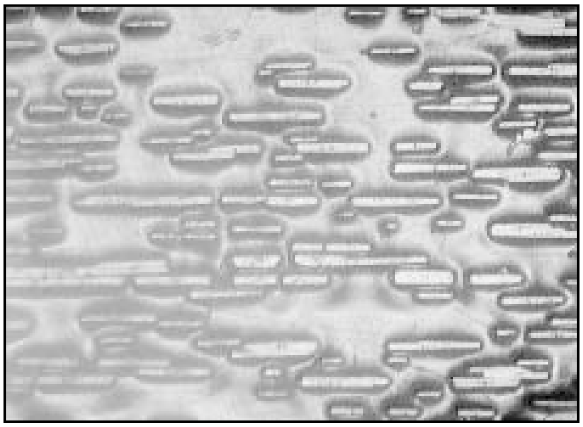


Figure 8—An example of dewetting. It was discovered that the undercoat had been wiped with a tack rag that had been dipped in solvent. The result was a streaky residue of plasticizer from the tack rag and oblong dewetted areas. Original photograph at 15X.

Defects Involving Volatiles

Popping, gassing, and air entrapment all are defects due to volatiles that cause bubbles and/or holes in coatings. The defect usually is obvious, but the cause is not. Popping occurs when solvent or other volatile materials in the paint are trapped as the film is formed, but blow out or form bubbles rather than diffusing out (see *Figures* 14,15, 23a and b). They can occur with any type of coating, but seem to be worse in waterborne coatings. That may be because of the inversion from an oil-in-water emulsion to a water-in-oil one that occurs on drying/baking. This change often traps water in the organic (oil) matrix that results. Waterborne coatings also have a tendency to skin which makes it more difficult for the water to escape. Then, on baking, it blasts its way out leaving a big hole.

Gassing refers to volatiles that come from the substrate, usually plastic or electrogalvanized steel. Bubbles and pores in plastic parts can blow out during the bake, leaving holes and/or roughness. Hydrogen and, possibly, methane can escape from in or under the zinc layer in electrogalvanized steel, producing defects that look just like solvent pops.[9,11] The paint usually gets blamed, but microscopy, especially of cross sections, can show whether it is the paint or the substrate (see diagram in *Figure* 16). There is a defect called pinhole cratering, pinhole gassing, or rupture (*Figures* 17 and 18) which is an electrodeposition paint and substrate problem.[11-14] It occurs in the form of pinholes, craters, bubbles, or roughness. With anodic electrodeposition, the cause of the bubbling and gassing is a process called Joule heating in which the deposition process heats water in the deposited paint so much that boiling occurs. Joule heating also happens in cathodic electrodeposition coatings, but the main cause is another process, electrical discharge, i.e., electric sparks that occur during deposition. These sparks blow holes in the paint film and can cause localized heating that can cure a ring around the hole preventing or reducing flow and further deposition. Hydrogen evolution and vaporization of water also occurs, both of which can give pinholes or pops (note the bubbles in the upper, unbaked electrocoat film in *Figure* 17). This defect occurs with cationic electrodeposition coatings when a certain voltage is exceeded. The magnitude of this threshold voltage depends on the substrate and is lowest for zinc-iron alloy coated steels.

Air entrapment is a problem with many coatings. Stirring, pumping, or spraying may cause air to mix in or dissolve in the paint. On application, the air tries to work its way out of the film, but often is trapped or the bubbles break late in film formation so that holes are left behind which do not flow out. The result may resemble solvent pops or gassing. Many coatings suffering from air entrapment look exactly like the pinhole gassing picture in *Figure* 18. Occasionally, so much air is trapped that the coating looks like foam.

Sometimes it is difficult to differentiate popping from cratering. Many pops are circular depressions with raised rims which is how we describe craters. Often the rims of pops are higher than those in craters (are more volcano-like), but not always. Pops that are the result of explosive blow-out of solvent may be deep crater-like holes

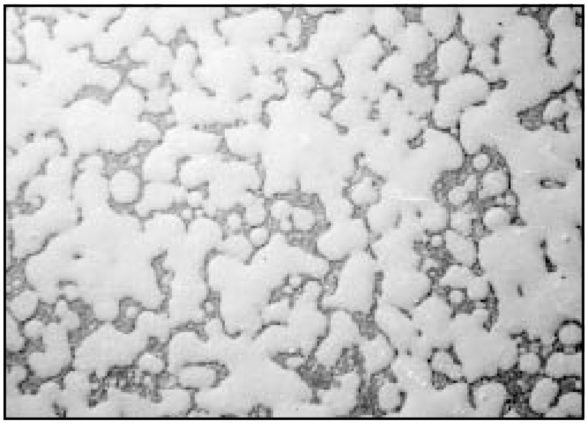


Figure 9—Poor knitting. This often occurs due to a combination of poor flow and poor wetting. Photograph taken at 10X.

Figure 10—An example of picture framing or fat edge in a coating for agricultural implements. Original photograph at 20X.

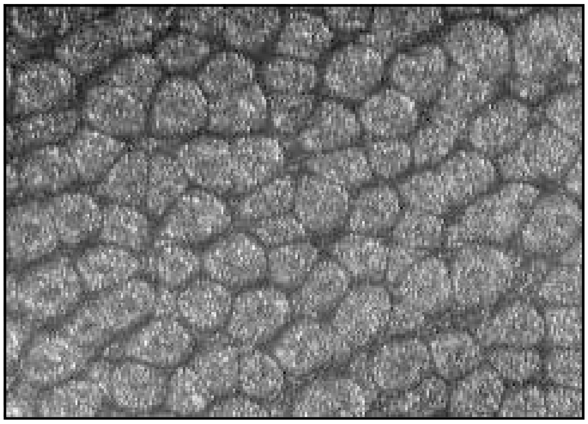


Figure 11—Benard cells in a blue metallic automotive topcoat. Photograph taken at 15X.

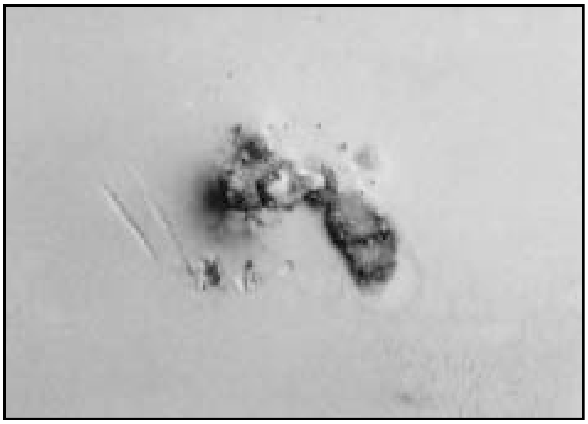


Figure 12—Clump of dirt in an automotive primer. Original photograph at 90X.

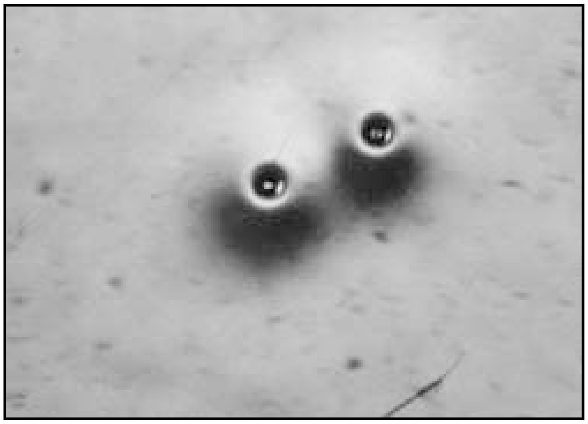


Figure 14—Example of a solvent pop. Note the volcano-like structures with clear domes with very small holes in them. Original photograph at 60X.

with no rim at all as in the cross section in *Figure* 19. Popping often gives at least a few bubbles or covered domes even if most of the defects resemble craters. Look at a number of the defects before coming to any conclusions. Some pops are small pinholes, so small that they can only be seen under the microscope. These micropops tend to give a dull, hazy appearance and/or poor gloss and poor distinctness of image.

Flow Defects

For application, film formation, wetting, and appearance, coatings must flow. Unfortunately, they have tendencies to flow too much or too little. Orange peel (*Figure* 1), which usually is due to lack of flow, is very common, partly because it gives a pleasing appearance to many objects and partly because it covers up or prevents other defects. Therefore, it is formulated into many coatings. Much of it is accidental, however, and may be due more to the application parameters than the formulation. A flow defect that seems to have become more common, especially with high solids coatings, is sagging. As solids have gone up, resin molecular weights have had to decrease (often to oligomeric levels), and resistance to flow after the solvent has gone also has decreased. High-solids coatings tend to flow and flow and flow. If the viscosity is raised to prevent sagging, then the appearance will be hurt and popping may occur. Because of sagging, different formulations may be used on vertical and horizontal surfaces of the same car body or other large object.

Telegraphing is a defect that usually involves both flow and dewetting. If a coating is applied over sand scratches, solvent wiped areas, or fingerprints, often the result is a highlighting or telegraphing through of the underlying marks, streaks, or spots (*Figures* 20 and 21). Instead of hiding what is underneath it, the coating advertises its presence! I have seen automotive metallic coatings where the aluminum flakes have aligned themselves along the sand scratches or wipe marks on the primer, leaving silvery streaks that can be seen from a considerable distance. This defect is not well understood and may have more than one mechanism, but it seems to be caused by dewetting and flow away from sharp edges (sand scratches) and areas of low surface tension (fingerprints and solvent residues, possibly sanded areas).

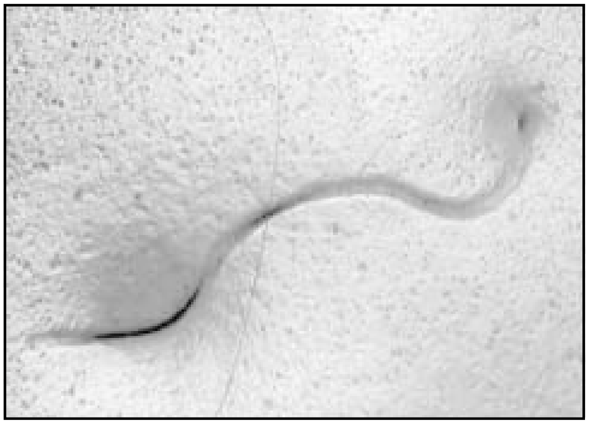


Figure 13—Fiber in an automotive primer. Photograph taken at 85X.

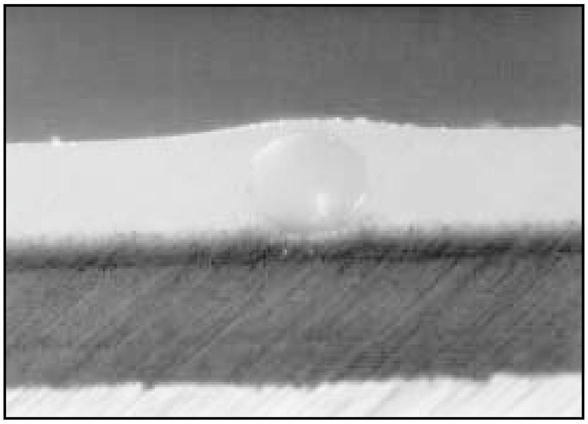


Figure 15—Cross section of a pop showing a large bubble in the clearcoat. This is not the same defect as in Figure 14, but the defect still was noticeable on the surface as a dome. If the bubble had burst, the result would have been similar to that in Figure 19. Photograph taken at 305X.

DIAGNOSIS

Identification

Identification of surface defects can be simple and easy or it can be complex and difficult, depending on the defect and the coating. I recently heard of some advice given by a medical school professor to his students: "Do not diagnose until you have carefully examined the patient and found out about his/her family history." This is good advice for diagnosing coatings defects as well. It is always necessary to examine the real, live defect (not a photo, not a written description, not the wet paint) before saying anything. Many people think that they can tell what a defect is just by looking at it with the naked eye. Often this is true, although a hand lens always helps. However, since the human eye can be fooled and observers often jump to conclusions, it is best to always look at defects with a light microscope, beginning with a low power (2-60X) stereo microscope. Sometimes it is necessary to do a cross section before the defect can be identified with certainty. I have been asked to work on a number of crater problems that turned out to be popping problems once the defects were examined under the microscope. The family history aspect mentioned in the quote also comes into play, both for diagnosis and root cause analysis. Find out as much as possible about the defect. Is this a new defect or has the paint been suffering from this malady for many years? Is the customer's plant notorious for dirt and other contaminants or is it noted for being clean? Are the work practices at the customer's plant good or bad? What application equipment is used, how well is it maintained, and what are the application conditions?

Root Cause Analysis

When a medical doctor completes his or her diagnosis, the cure often is clear and a standard course of treatment follows. When a coatings defect has been diagnosed, another step usually must be completed before the problem can be attacked. That step is the determination of the root or basic cause of the defect. Knowing that there is a cratering problem does not tell us why the paint is cratering or what the causitive agent is. The root cause may be a badly mixed component, a contaminant, or the wrong solvent in a paint batch. It may be a faulty piece of application equipment, a faulty process, or it may even be poor supervision. The idea is to identify the cause and prove that it is the cause. Guessing is not good enough. You must have data to prove that it is the root cause. Root cause analysis demands more discipline, experimentation, and documentation than is normal in North American problem solving, but it is necessary if the problem is to be truly solved and its reoccurance prevented.

Root cause analysis is a science in itself and has been the subject of many lectures and even short courses. I will not spend a lot of time on it, but I can illustrate its use with a case study. This problem involved solvent popping in an auto base/clear system. Popping is rare on this line because film thicknesses usually are at the low end of the specification. The defects were ugly blow-

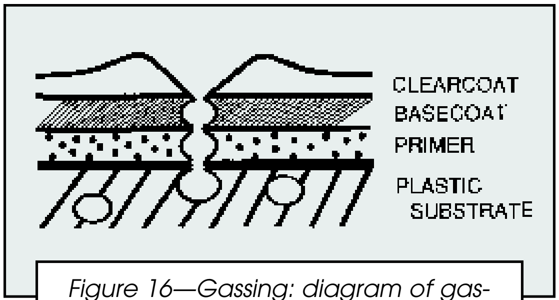


Figure 16—Gassing: diagram of gassing from a void in a plastic substrate. Galvanized gassing gives a similar set of bubbles originating in a blister or flap in the zinc layer.

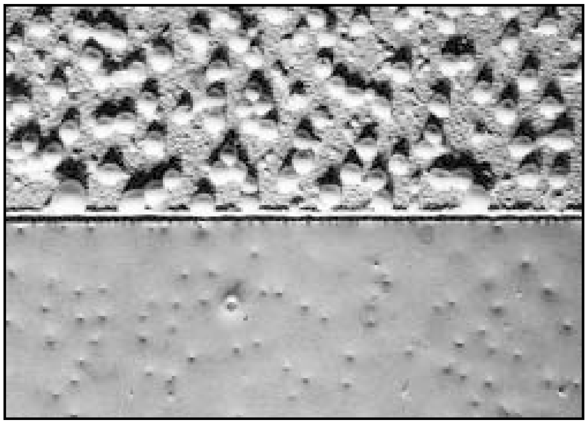


Figure 17—Pinhole gassing: unbaked (top half) and baked (bottom half) electrodeposition primer films over galvanneal zinc-iron alloy coated steel. Photograph taken at 7X.

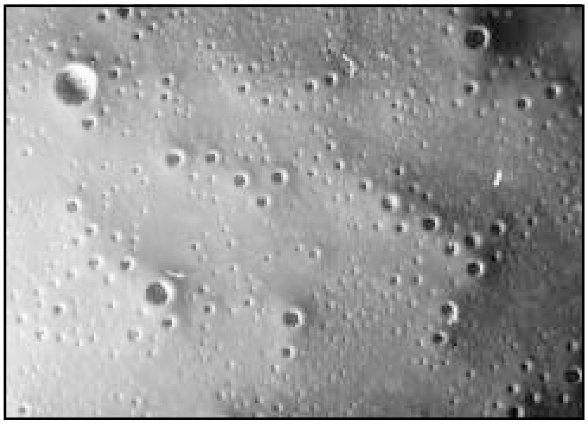


Figure 18—Pinhole gassing: acrylic electrocoat over galvanized steel. The rupture voltage had been exceeded and there was excessive gassing. Original photograph at 15X.

Figure 19—Cross section of a blowout pop which originated in the basecoat or clearcoat. Photograph taken at 152X.

out type pops that looked like miniature volcanoes with small amounts of yellowish "lava" flows (material that had welled up from the center). The techniques used to determine the root cause were light microscopy of the defects (both surface and cross sections) and scanning electron microscopy and its attached X-ray spectrometer (SEM/EDX) to identify elements in the pops. These elements turned out to be those found in the pigments in a repair primer which was sprayed on areas where sanding had gone through the primers to or close to the metal. We determined that the root cause was repair primer overspray. Large overspray droplets trapped solvent which blew out in the oven after topcoats were applied. The "lava" was the repair primer blowing out through the topcoats. We presented a number of light microscope and SEM pictures to the customer along with the report. The customer then did something unusual, but extremely useful with this material. Posters were made from our report and pictures and then were hung outside the spray booths to show the line workers why they should minimize repair primer overspray. It made me realize that we do a lot of telling people what to do and what not to do, but we rarely tell them why or illustrate the consequences of their actions.

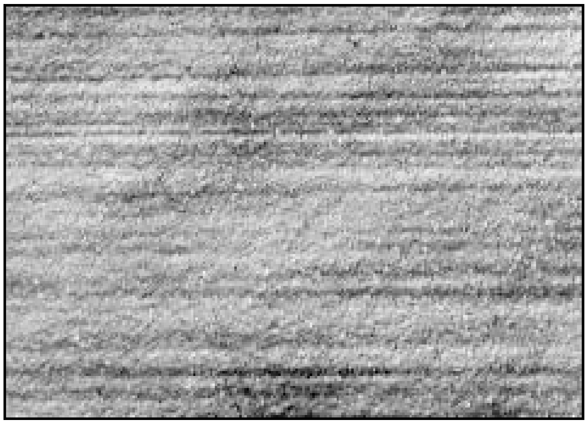


Figure 20—Telegraphing of sand scratches through an automotive silver metallic coating. Original photograph at 22X.

I recently spent nearly three weeks at a customer's plant and our nearby satellite plus a number of days in my own lab working on a cratering problem. We had support from several analytical labs, including that of the customer. I think that we finally have established one root cause, but there may well be more. It is not unusual to expend this kind of effort and to have even less to show for it than in this case.

Techniques Used in Root Cause Analysis

Observations: The most useful single tool for root cause analysis is the light microscope, but there are many other tools and techniques. One technique is to observe the defect as it happens. There are advantages in having lab people visit customer's lines any time (the more they know of the customer's equipment and process the better), but it is even more useful to have the lab person personally observe a problem on line. Another useful technique is to recreate the defect in the lab. Even if a contaminant has been identified in a defect or a certain solvent identified as the culprit in a popping problem, it is wise to check this by reproducing the problem using that material. If you cannot produce craters with the contaminant or adding more of the suspect solvent does not make popping worse (or it does not occur at all), then the cause probably is something else.

A useful technique is to apply the paint to a small coupon which is placed on a hot stage to observe (usually with a microscope and/or videocamera) the formation of defects on baking. If an oven with a window is used, observations can be made of the baking of panels or parts with a camera or a microscope/telescope with a long working distance. Transmitted light microscopy of wet paints can be useful to determine dispersion quality, whether seeds or dirt are present, and whether the paint has a tendency to trap air. Microscopy is particularly useful for examining waterborne paints because even as resins or clears they are multiphase systems with observable characteristics. Changes in dispersion quality, latex or micelle particle size, degree of flocculation with time, temperature, addition of solvents, changes in formulation or order of addition, etc. are readily apparent and can be monitored on a regular basis. For example, *Figure* 22 shows the effect of heat aging on a waterborne coating. The dispersed resin micelles have coalesced with time to form larger particles and stringy globs.

Examination of cross sections of defects with a higher power (100-500X) microscope can be very useful for determining what the defect is, identifying dirt particles, and locating the origins of popping. *Figure* 23 gives a good example of the last-named use. The defects shown were in a silver metallic base/clear system and looked like little dark spots or nodules, sort of coatings measles. From the surface (*Figure* 23a), it appeared that the problem was in the basecoat, but a cross section (*Figure* 23b) indicated otherwise. The pops (or eruptions, to describe them more accurately) were in the primer.

One problem with putting a lot of emphasis on observations and making decisions based on comparing lab-produced defects with those from the field is that there is a tendency to assume that defects are constant and

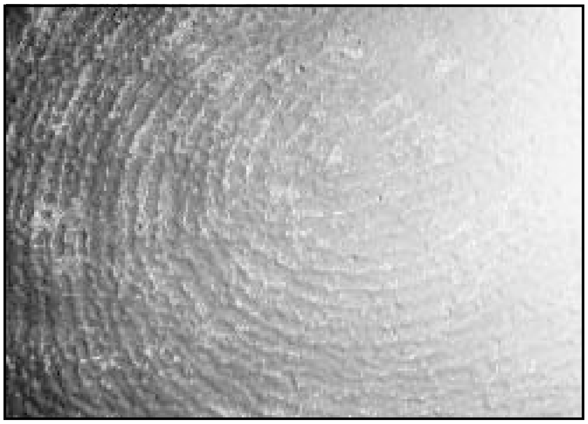


Figure 21—Telegraphing of a fingerprint through an industrial coating. Photograph taken at 11X.

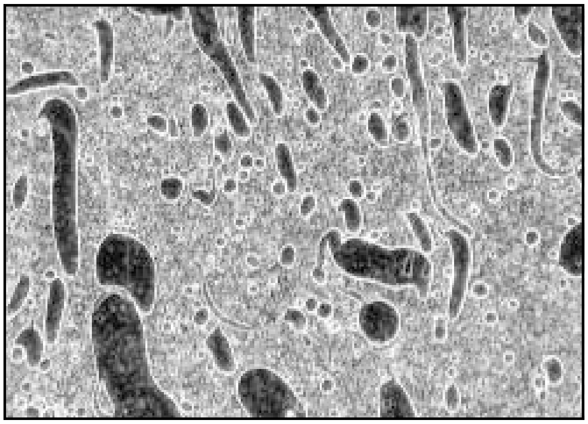
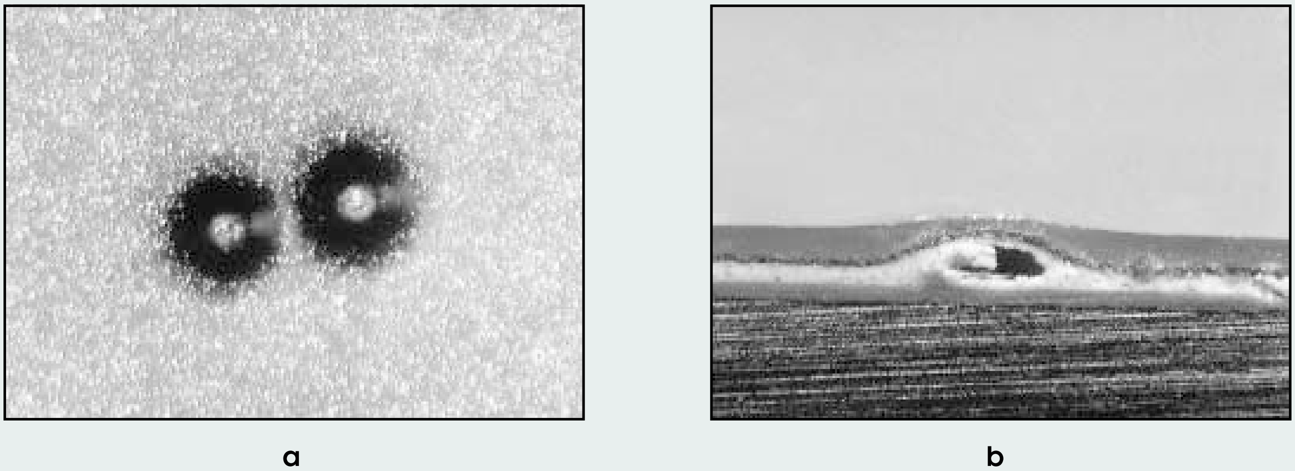


Figure 22—A waterborne coating with a stability problem as seen through the microscope using transmitted light. The resin micelles have coalesced to form larger droplets and stringy globs. Original photograph at 382X.

unchangeable. For example, some people classify craters according to size, shape, depth, etc., and come up with labels such as A-1 or B or X. That is fine, but, then they assume that a given contaminant will always give type A-1 craters. This is not true! Even in a given coating, a certain contaminant may produce shallow craters under one set of conditions, deep ones under another set, and no craters at all under yet another set. Defects are variable just like any other paint property.

I have spent much time over the last three years working on dirt problems in customers' plants. It takes a lot of detective work, a lot of microscopy and analytical work between visits, and a lot of cooperation from the customer. Sometimes the poor practices and dirt sources jump out at me, other times they are so well hidden that it takes several visits to identify even a few of them. Usually the on-site service people are aware of many of the problems, but the customer rarely listens to them. That should be a lesson to you—listen to people who are on the line every day! I certainly do. The main tools in solving dirt problems are the human eye (walking through the customer's line and looking, looking, looking) and a microscope. It is very useful to carry out a dirt survey or audit to pick up typical dirt, locate dirt sources, identify problem areas, note questionable work practices, etc.[15] It is important to take detailed notes and collect dirt samples as you go. A detailed investigation may take a week or more.

A very important aspect of observation is documentation by photography and/or videotaping of defects, cross sections, wet paint, and defect recreations, usually with a microscope, but a camera with a 100 mm or 200 mm macro lens can be effective as well. Photographs are very useful as permanent records that can be pulled out of files (computer or otherwise) to settle arguments and answer questions. A dirt library (photographs of known dirt specimens) can be helpful in identifying unknown dirt. There are commercial computer programs that enable a person to capture images of known material and



a

b

Figure 23—Popping defect in an automotive silver metallic base/clear system: (a) as seen from the surface (75X); (b) in cross section (152X).

defects and store them for comparison to unknowns at a later time.[16] Some have a split screen mode so that an unknown can be compared to a series of knowns and the best match determined. There is an important caveat when using a dirt library: you can only match materials if you have excellent images of clean (i.e., not covered with paint) pieces or particles. Often what is trapped in the paint film is a lump that could be anything. A quick look and comparison to a photo or stored image will not identify the dirt. Careful removal (which takes a lot of skill) may be necessary[9,15] or a cross section may have to be done in the lab (*Figure* 24). An IR microscope or SEM/EDX may be needed for complete identification.

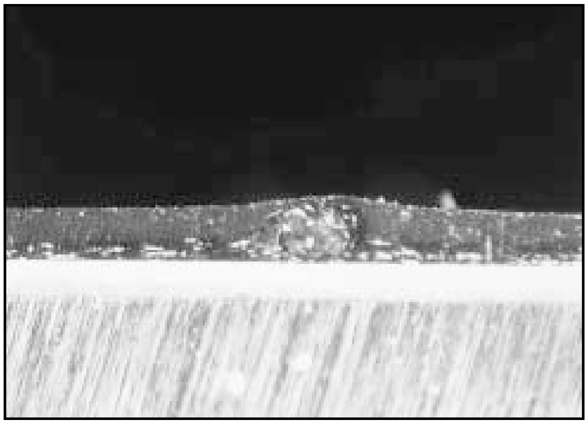


Figure 24—Cross section of an automotive coating system with a piece of dirt trapped in the basecoat. Photograph at 152X.

Wettability Tests: Most wettability tests are based on determining the angle of contact of drops of liquid (paint, water, solvent) that have been placed on the surface of interest (*Figure* 25).[1,8,10,17-19] The lower the angle, the better the wetting. Perfect wetting gives such spreading that there essentially is no angle at all. There are two kinds of contact angles, advancing and receding. The advancing angle is the more common and is measured as or after the drop advances across the surface. The receding contact angle is noted when a drop retracts over a previously wetted surface.

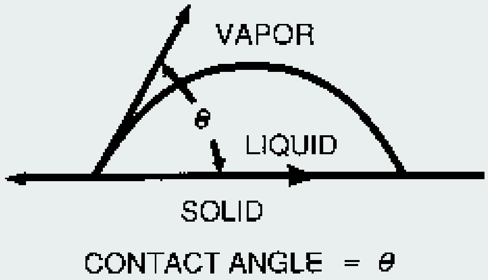


Figure 25—Diagram of a contact angle drop.

The contact angle of a single liquid on a surface may be useful, but does not tell us the surface tension of that surface. One test that can provide a surface tension involves measuring contact angles of a number of liquids on the surface and using Zisman plots[1,8,10,17] of the cosine of the contact angle vs. the surface tension of the drop liquid to determine critical surface tensions. See *Figure* 26 for a Zisman plot for the wettability of polytetrafluoroethylene (PTFE) by n-alkanes.[10] The intercept of the line or curve with cos θ = 1 (contact angle = 0 deg) gives the critical surface tension, γ_c. As long as the surface tension of a paint is less than the critical surface tension of the surface to which it is applied, the paint will spontaneously wet the surface and spread over it. Zisman plots can be useful, but they often are curves or the data is scattered which makes extrapolation difficult. Also, there are a lot of problems that critical surface tensions do not explain. Dewetting Zisman plots based on receding contact angles would seem to be useful, but rarely have been done in the coatings industry. *Figure* 27 shows both advancing and receding Zisman plots along with surface tension regions for spontaneous wetting and dewetting.

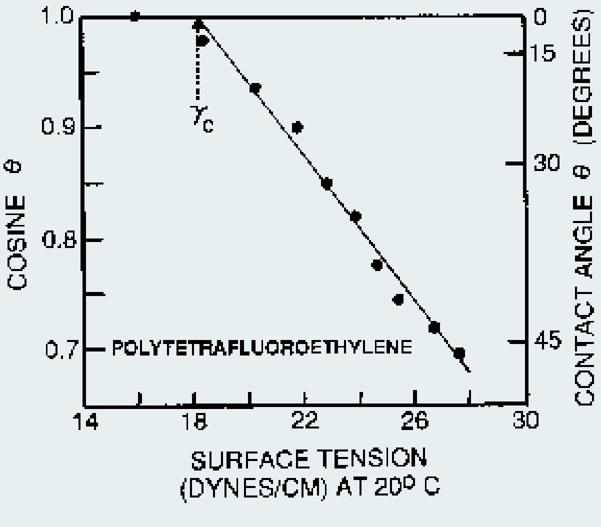


Figure 26—Critical surface tension (Zisman) plot for wettability of tetrafluoroethylene by n-alkanes,[10] γ_c is the critical surface tension.

A simple swab test for estimating the critical surface tension was developed many years ago by Hansen.[20] This wetting/dewetting test is easy and quick and can be employed in the field or at a customer's plant. It works on curved and irregular surfaces where accurate contact angles cannot be measured. Cotton swabs and a series of solvents of known surface tension can be used or surface tension "pens" which make the job even easier.[21] The basics of the test are to swab the solvent onto the substrate and observe whether the strip of solvent stays in place or dewets (crawls or retracts). The surface tension of the highest surface tension solvent that wets the surface without dewetting is taken as the critical surface tension of the substrate.

Figure 27—Critical surface tension (Zisman) plots for advancing and receding contact angles.

Water contact angles by themselves are used to estimate surface cleanliness after cleaning operations, ease of wettability of surfaces by waterborne coatings, and the effectiveness of rinsing processes. Sometimes the test is a very simple running of water across the surface to see whether the liquid sheets off or beads up.

More recently, solid surface tension models in which the surface tension is composed of two components have become popular. In one, the Owens-Wendt-Kaelble,[1,8,22,23] the two components are dispersion and polar and the solid surface tension is

$$\gamma_s = \gamma_s{}^d + \gamma_s{}^p$$

Contact angles are measured with two liquids, such as methylene iodide and water, and values are substituted into the Owens-Wendt-Kaelble equation

$$\frac{\gamma_l(1+\cos\theta)}{2} = (\gamma_l{}^d\ \gamma_s{}^d)^{1/2} + (\gamma_l{}^p\ \gamma_s{}^p)^{1/2}$$

where γ_l is the surface tension of the liquid and γ_s is the surface tension of the solid. We end up with two equations (one for methylene iodide, the other for water) in two unknowns which we solve to determine components and the total solid surface tension.

Table 1 and *Figure* 28 present solid surface tension values for specimens of an acrylic coating with differing amounts of a silicone surfactant. As more silicone is added, the dispersion component goes up and the polar component goes down. The surface becomes less and less polar as more of it is covered by the surfactant. Above about 0.2%, further silicone has no effect because the surface is completely covered. The total solid surface tension goes up and down within a small range. This is one way to determine how much surfactant is enough.

Table 1—Effect of Silicone Surfactant on the Solid Surface Tensions of an Acrylic Coating with a 40 min Bake at 300°C

	Solid Surface Tension, Dynes/cm		
Percent Silicone Surfactant	Total	Dispersion	Polar
0	41.9	35.2	6.7
0.01	43.2	37.6	5.6
0.10	39.0	38.0	1.0
0.15	39.9	39.3	0.6
0.25	41.6	41.1	0.5
0.35	40.7	40.0	0.7

Table 2 shows results of testing related to a problem of poor wetting of topcoats over a certain primer after it was aged. Contact angles were measured on an aged specimen of the primer, the same after washing with a detergent solution and carefully rinsing with water, and on a control (similar primer known to give good wetting). The values shown in *Table* 2 indicate that the unwashed problem primer was considerably more polar than the other two. This pointed to a polar exudate on the surface of the problem primer. Further investigation showed that the polar crosslinker was not reacting in completely and was slowly coming to the surface.

Comparison of recent results with the swab test (at a plant, using a limited number of solvents) and the O-W-K technique in the lab show that they can give similar results (see *Table* 3). The swab test values tend to be lower than the total solid surface tensions, but they clearly show the differences in the coatings. Primers A and B were more difficult to wet and were more sensitive to contaminants than primer C in terms of allowing topcoat cratering. The topcoat was included because it was noted that it recoated well and virtually never gave craters when a repair coat was applied. It also had a polar component that was similar to that of primer C. There is some evidence that such a match gives superior adhesion.[24]

The two-component surface tension does a better job of explaining defect and wetting problems than do Zisman plots, but certainly does not explain everything. Sometimes, the only way to see how good the wetting of a substrate is to measure contact angles of drops of the

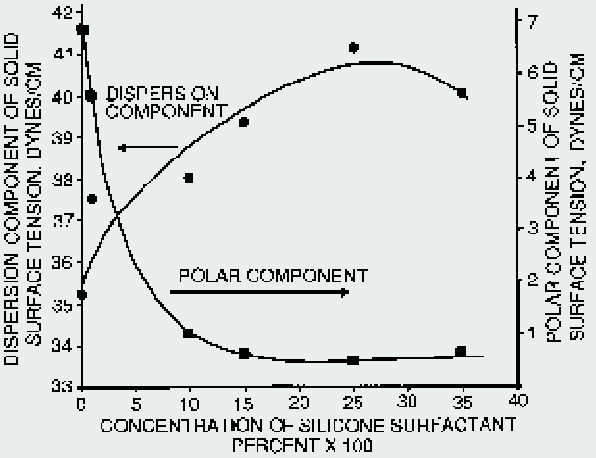


Figure 28—Solid surface tensions versus percent silicone surfactant for a series of industrial acrylic coatings.

Table 2—Primer Problem: Solid Surface Tensions of Aged and Washed Primers Compared to a Control

	Solid Surface Tension, Dynes/cm		
Specimen	Total	Dispersion	Polar
Aged problem primer	44.9	30.3	14.6
After washing	46.4	40.0	6.4
Control	44.0	37.3	6.7

Table 3—Critical Surface Tensions by Swab Test and Solid Surface Tensions for Three Primers and a Topcoat

	Critical Surface Tension	Solid Surface Tension, Dyne/cm		
Coating	By Swab Test, Dynes/cm	Total	Dispersion	Polar
Primer A	32	34.5	28.7	5.8
Primer B	31	33.4	27.3	6.1
Primer C	40	45.1	41.3	3.8
Topcoat	36	40.9	36.8	4.1

paint on the substrate or to spray a thin coat of paint on it. A wetting index can be determined from the latter test by determining the applied paint thickness that will just give complete coverage. Formulations or batches can be compared. Lower values mean better wetting.

Solid surface tension also can be separated into three components, γ^d, γ^p, γ^h (dispersion, polar, and hydrogen bonding, respectively). These can be established by measuring contact angles with three pure liquids[24,25] or by wetting studies with a larger series of liquids.[26,27] The reader may notice the similarity between the surface tension components and three-dimensional solubility parameters. Indeed, there is a close relationship between these two properties,[28-33] and a solubility parameter plot can be converted to surface units.[26-32] A solubility parameter plot of the surface of polypropylene based on contact angles and spontaneous spreading is shown in *Figure* 29.[26] Such measurements are very tedious, but can be useful.

Osterhold and Armbruster[34] have applied a different concept based on the theory of Good and co-workers[35] where there also are three components, but they are γ^{LW} (Lifshitz-van der Waals), γ^+ (electron acceptor), and γ^- (electron donor). The latter two can be thought of as forming an AB component resulting from acid-base interactions. Osterhold and Armbruster showed that clearcoat wetting of a dried basecoat correlated well to γ^{LW}, but not to the O-W-K results or the acid-base components.

An important caveat with all these physical techniques is that they can signal that a surface is contaminated or difficult to wet, but chemical analysis techniques must be used to determine the cause of the problem. Another point is that wetting measurements are done at equilibrium and at room temperature, whereas paint application and subsequent effects are dynamic processes and temperatures may be lower and higher than room temperature over a short period of time.

Analytical Instruments/Techniques: Many analytical techniques have been used to identify contaminants, characterize solvents and other components, etc. Examples include the scanning electron microscope and X-ray attachment (SEM/EDX),[9] Fourier transform infrared spectroscopy (FTIR),[36] chromatography, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS or ESCA),[37-39] and time-of-flight or static secondary ion mass spectrometry (TOF-SIMS or SSIMS).[38-41] XPS and SIMS are very expensive, very powerful surface analysis tools that have had some success identifying small amounts of residues in craters. Such tools are too expensive for most companies to buy, but there are laboratories that do such analyses on a fee basis.

Viscosity Measurements: Many defects involve flow of some kind, so it is not surprising that viscosity measurements can be useful in determining causes of problems. The question is, the viscosity of what? Some people try to predict paint behavior from the viscosity in the can, but that certainly is not what is on the car, washing machine, piece of furniture, etc. One method is to apply the coating, then scrape it off and determine its rheological behavior. This is a lot of work and most people find that the application itself is sufficient to show whether the coating is acceptable or not. However, measuring the viscosity can show us why the paint performs the way it does. Another technique is rolling ball viscosity[42,43] in which paint is applied to a panel which is placed on an inclined plane and a small metal sphere (ball bearing) is rolled down the wet panel every 30 sec or so until the paint sets up. The inverse of the velocity of the ball is a measure of viscosity. *Figure* 30 shows surface (rolling ball) viscosity curves for three clearcoats. The original formula (greatest increase in viscosity with time) gave too much orange peel and a tendency to pop. Addition of a flow control agent reduced the rate of increase of viscosity and improved performance, but partial replacement of one of the solvents with a slower one had a greater effect. *Figure* 31 provides curves for a series of basecoats, some of which cratered, others of which did

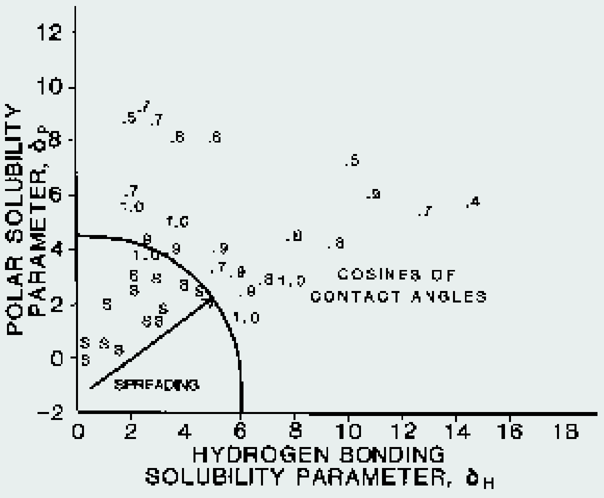


Figure 29—Wetting of polypropylene: wettability as a function of the solubility parameters of the contacting liquid.[26]

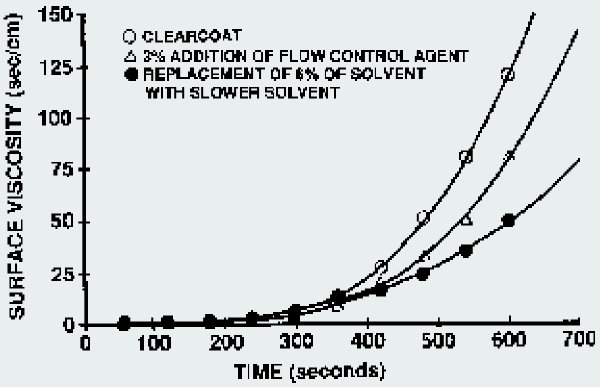


Figure 30—Surface (rolling ball) viscosity versus time for an automotive clearcoat before and after modification with a flow control agent and by adding a slow solvent. Quarter inch (6.35 mm) ball bearing, 15° angle, 20°C.

not. The ones that took a long time to increase in viscosity after application were more apt to crater.

Another method is microdielectric analysis which has shown promise for characterizing film formation and cure.[44,45] In this technique, the paint is applied to a thin, flat sensor placed on the substrate, then flashed and baked normally. The sensor monitors the dielectric properties of the paint film at and near the interface between the sensor and the coating. The main dielectric parameter used is called ion viscosity, but really is electrical resistivity rather than a true viscosity. Ion viscosity is a measure of both the mobility and number of ions in a specimen. It is affected by changes in temperature, loss of solvent, crosslinking and other chemical reactions, formation of physical structure (such as by a thixotrope), ionic impurities, and ionic additives. Although an ion viscosity vs. time trace often parallels true viscosity behavior during the solvent flash and bake, ion viscosity is not a measure of the flow properties of the coating. Therefore, care must be taken in interpreting dielectric analysis data. However, this is more than made up for by the fact that the measurements can be made in-situ under normal flash and bake conditions.

Figure 32 provides a good example of the kinds of plots and comparisons that can be made with this technique. It shows ion viscosity behavior as a function of time during solvent flash and bake for a solventborne acrylic clearcoat at three bake temperatures.[45] Note that the higher bake temperatures give lower ion viscosity minimums, but a shorter time at or near this minimum. A higher bake gives more initial flow to allow final leveling, but the coating sets up faster which should reduce later, unwanted flow. The rate of increase after the minimum corresponds to the cure rate and is higher for the higher bakes. High temperature cone/plate viscosity measurements can be used to follow cure, but do not allow solvent loss, so do not give a realistic picture of what happens in the oven.

Microdielectric analysis also can show the overall effects of paint film interactions such as in wet-on-wet applications which are difficult or impossible to characterize with other techniques. An example is shown in *Figure* 33 which contains ion viscosity and temperature plots for an experiment in which a clearcoat was applied over a partially dried basecoat.[45] The basecoat was applied and the ion viscosity increased as it began to dry. After about five minutes, the clearcoat was applied over the basecoat which caused the ion viscosity of the system to decrease. The ion viscosity then increased until the panel was placed in the oven, after which time normal curing behavior was seen. Again, other techniques could be used, but none of them give as much of the total picture from application to the end of the bake as this technique.

In other work, impedance measurements have been used to monitor dielectric behavior (ionic conductance) in order to follow film formation of a latex floor polish coating at varying levels of humidity.[46] Using this technique or microdielectric analysis, drying and/or baking data could be generated for a series of formulations and compared to the tendency to form surface defects. Formulations then could be designed with optimum drying/baking behavior to mimimize defects.

SOLVING SURFACE DEFECT PROBLEMS

Now that we have discussed a number of different defects and how they can be identified and their causes determined, let us consider how we can move the defect resistance properties of coatings closer to what our customers expect and demand.

Countermeasures

Once the root cause has been established, then countermeasures, i.e., actions to solve the problem, can be taken. If a contaminant in the customer's plant has been identified, work with the customer to get rid of it. If the batch was made incorrectly, institute procedures so this will not happen again. If the formula is too sensitive, change it to make the paint more robust (which is much

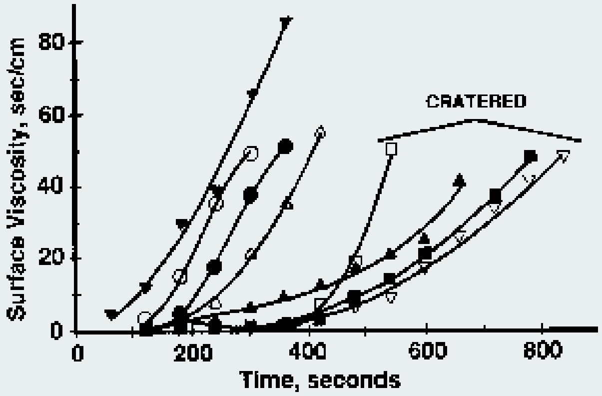


Figure 31—Surface (rolling ball) viscosity versus time for a series of automotive basecoats. The coatings with low rates of increase in viscosity with time cratered on application, those with high rates did not.

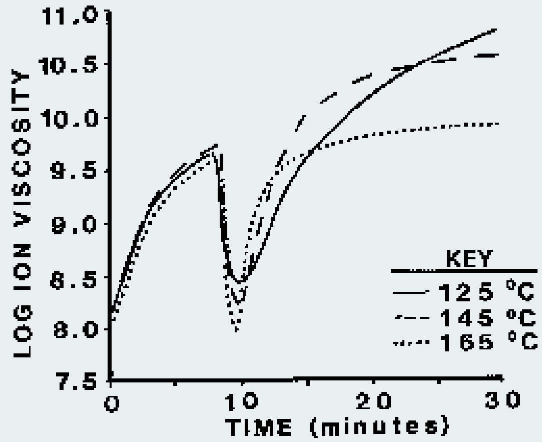


Figure 32—Log ion viscosity during processing of an automotive solventborne acrylic clearcoat at three different bake temperatures.[45]

easier said than done). Many defects can be prevented or controlled by very careful balancing of rheology, surface properties, and cure kinetics. Cleanliness in the paint plant and on the customer's line also are very important.

There are many additives, but no magic ones. Too often people want one material that they can add at a low level to solve a problem. "Give me some fu-fu dust." Searching for that one perfect miracle additive takes time away from doing experiments to find out what the problem really is and the combination of measures needed to solve it. Additives certainly are important. The right additive package can go a long way toward solving a problem, but additives must be chosen and tested very carefully. They often help one problem, but cause another by degrading other properties. Some additives work very well in only one paint system, others in several systems, but very few are universal. Combinations of additives usually work better than individual ones. For example, both flow control agents and surface active materials are needed to prevent many defects. Too often, the additive package is an afterthought and causes other problems such as poor appearance. Additives can work together or interfere with each other. If the additives are formulated in from the beginning, it is easier to work around the difficulties. It is wise to seek help from additives suppliers who develop materials to counter specific problems, but it still is necessary to do trial and error work to determine the best additive combination for a given paint and to discover any problems before going on line. See references 1, 8, 19, 47-50 for suggestions on additives. Much more information may be found in suppliers' literature and the general coatings literature.

CRATERS AND OTHER DEWETTING: Removal of contaminants is the best way. If a material used in a customer's plant causes craters in the lab, get that material out of the plant if at all possible. If oil is dripping on the ware, stop the drip or install a drip pan over the line. Sometimes, no cause can be identified or the suspect material cannot or will not be removed. In those cases, the formulation must be made to be more robust. Improving the resistance to contaminants is difficult, but can be done by very carefully balancing rheology and surface properties. Thickeners, thixotropes, flow control additives, and surfactants commonly are used to accomplish this.

DIRT: Solving of dirt problems usually involves a lot of detective work in the lab to identify the dirt on panels and parts run through the customer's line and in the customer's plant to find out where the dirt is coming from. It may be a dirty substrate, washers not working properly (plugged nozzles, for example), poor E.D. primer agitation that allows settling, dirty paint, dirt from a neighboring factory or power plant, or dirt generated by operations within the plant, particularly sanding. Once a source is found, it can be removed or isolated. If it is a process problem, such as excessive overspray, then the process must be changed. Dirt prevention usually demands a paint shop separated from the rest of the factory, a separate air system for the paint shop, enclosed booths and tunnels within the paint shop, filters galore (and the right filters) – everything to keep what's inside in and what's outside out. Even then, daily cleaning is necessary in application areas and weekly cleaning in ovens. Periodic deep cleaning of the whole line can be useful, but often gives an initial increase in the dirt level because so much dirt has been loosened and stirred up. Dirt in the paint can be removed by filtering and prevented by a high level of cleanliness in the paint plant, good manufacturing practices, and clean drums, totes, and tank wagons.

POPPING AND OTHER VOLATILE-RELATED DEFECTS: Solvent popping usually is attacked via changing the solvent package in the paint, although slowing down of cure to prevent skinning and allow solvents to escape, using additives that act like boiling chips to release volatiles, reducing film thickness, applying in multiple passes, and applying a drier spray (which can help or hurt) are other things that can be done.

FLOW-RELATED DEFECTS: The rheology of a coating can be changed in many ways and to counter many prob-

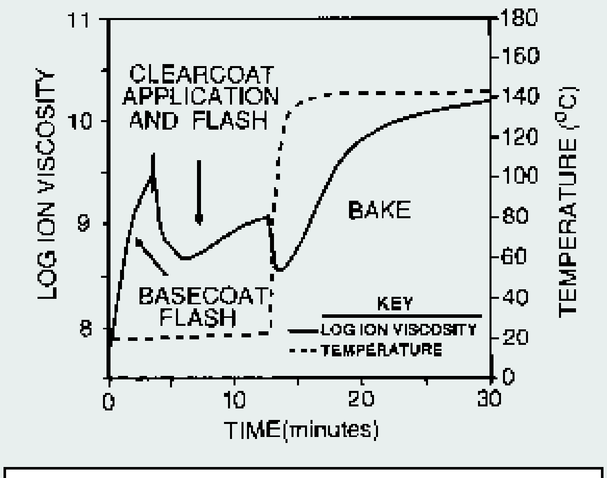


Figure 33—Log ion viscosity and temperature during processing of an automotive clearcoat/ basecoat applied "wet-on-wet".[45]

lems. Sagging and other unwanted flow can be reduced or prevented by building in structure with thickeners or thixotropes to raise low shear viscosity. Flow and leveling can be improved by lowering the low shear viscosity and the use of flow control additives. By controlling the rate at which structure forms, both leveling and sag resistance can be achieved. The idea is to have sufficient flow for leveling, but then to prevent the occurrence of further flow (it is not easy, but it can be done).

Documentation: Once a defect has been cured, the details of the investigation and the countermeasures (and their success or lack of it) should be carefully documented for management, personal files, and the customer. Ideally, the report should be in some retrievable form (library catalog, computer file/catalog, etc.) so that other problem solvers can access it when similar defects are encountered in the future.

BARRIERS TO CURING DEFECT PROBLEMS

You may say that you are doing all of these things, yet you are still plagued with defects. There are a number of possible reasons for this, some technical, some non-technical, or only partly technical.

Technical Barriers to Curing Defect Problems

Lack of Adequate Tests: Some defects continue to occur partly because we do not have good tests to see whether paints are resistant to giving the defect or not, especially under the conditions in the customer's plant. An example is cratering. It is frustrating and puzzling that paints crater so easily at a customer's plant yet are so crater resistant in the lab. Paints that crater on line rarely crater in the lab, no matter how many panels are sprayed. Having a test that reliably predicted whether the paint would crater at the customer or not would be very useful. Instead, it may be necessary to use the customer's factory to test paints and changes in them. This is not recommended, but sometimes must be done. One of the reasons is that it is so difficult to recreate the customer's equipment and conditions in the lab.

We have the opposite problem with dirt. Panels are much more apt to show dirt in the lab than car bodies or appliances are in the plant. Paint labs are dirty compared to most factories. This means that if a paint picks up dirt in the lab, you do not know if the paint will be a worse dirt catcher than most or not. Popping is another defect that is not always easy to predict from lab panels. Popping may not occur in the lab, but a styling crease, corner, or other design peculiarity on a car body, washing machine, piece of metal furniture, etc., may end up with enough paint such that popping does occur. Flow problems are difficult to predict without applying the coating in the same manner as at the customer. This is less of a problem for Quality Control than it is for formulators who end up spraying thousands of panels and would love to have viscosity measurements that give reliable predictions of flow, leveling, sagging, and resistance to cratering.

Unusual and/or Severe Contaminants: Sometimes a contaminant is so unusual or so powerful that it causes the most robust paint to crater or dewet. Once identified it usually can be removed, but residues may cause defects to occur for days or weeks. For example, silicone gaskets in air lines, paint lines, and pumps have caused severe and long-lived cratering in a wide range of coatings. New components, parts, adhesives, or sealants on whatever is being painted can also cause defects. Customers often offer these for testing for paint compatibility before they begin using them, but sometimes they forget. Very fine dirt also could come under this heading. Airborne dirt or dust particles so small that they can be seen in the air only in bright light may form quite visible defects in or on a glossy coating.

Unacceptable Countermeasures: With many coatings, craters could be stopped immediately by raising viscosity, especially low shear viscosity, but at the cost of severe orange peel. That might be all right for an appliance coating, but would be unacceptable for an automotive coating. In another case, a surfactant may be added to a paint to improve wetting of a substrate, but with the unfortunate result that the coating cannot be repaired or recoated. As much surfactant comes to the air-coating interface as to the coating-substrate interface and the coating surface becomes almost as difficult to wet as a Teflon pan. A countermeasure for many appearance problems is to put on more paint, but a thicker coating often gives popping. Reducing thickness to prevent popping may lead to poor knitting on spraying or give a ropey appearance on roll coating. Most automobile paint lines have ovens that begin with infrared (IR) sections in order to set the surface so that oven dirt will not penetrate and stick to the coating. Unfortunately, the skin that forms can also cause popping.

Nontechnical Barriers

Lack of Adequate Training: The more training that service people (from both producers and users) have, the better chance that the defect will be recognized, the root cause determined, and the problem will be solved on-site. Poorly trained people can fail to recognize defects and/or causes, be defensive, block communication, and make problems worse. Money spent on training almost always saves money later on. It is a matter of "pay me now or pay me later." This extends to line workers. If the paint supplier's workers are well trained, they will know why cleanliness in the paint plant is important and that contaminants can cause seeds and craters. If the customer's workers are well trained, they will know why careful surface preparation is important and they will know how to do it. They will know why good application practices are important and how to do them. The paint supplier should train his workers, but also should participate in the training of his customer's workers. The supplier can teach best application practices, how to avoid dirt problems, how to look for defects, etc. Another aspect of training is that it is a way to make sure that everyone uses the same terms to describe defects, understands the tools and techniques for diagnosis, and knows what various countermeasures entail.

Communications/Relationships: Good communications between customer and paint supplier are critical to solving defect problems. Ideally, both should be part of the team. That means that the relationship between the two must be good. An adversarial relationship is very bad for problem solving. Sometimes the issue is lack of recognition by the customer of his/her part in the prevention of dirt or other defects. If I arrive at a customer's plant and am told that "you have a dirt problem," then I know I am in trouble. If the problem is not shared, it will not be solved, or it will take a very long time to solve. Lack of cooperation from a customer regarding implementation of the things that need to be done to prevent or solve a problem can make life very difficult for a supplier who is told "fix the problem, but do not change anything." The customer may have a condition in his plant that you believe contributes to the problem, but unless he accepts this, you are going to have a tough time changing it. This is where good detective work backed by careful lab experimentation and testing to provide strong evidence is necessary. Even that is not always sufficient to convince a customer who does not wish to believe your conclusions as to the cause.

I think that single sourcing (all paint in one plant from one supplier) can contribute to supplier-customer trust and cooperation, but it does not guarantee it. I have been in single-sourced plants where we were considered the enemy and others where there was excellent team work. Regardless of sourcing, there is more sharing of information and more chances for creative solutions when the supplier and customer work closely together and trust each other.

Ironically, poor communications within a raw material supplier, paint company, or paint user can be a bigger barrier than those between producer and user. I think that an important job of any raw material or paint supplier is to keep individuals at a given customer up to date on what the rest of the labs, plants, etc. of that customer are up to. Problem solvers often fulfill similar needs within their own companies and for customers. Sometimes the poor communication occurs because a lack of clear responsibilities. For example, cleaning or application equipment may be malfunctioning, but noone asks maintenance to fix it or requests that money be budgeted for new equipment. I have seen paint problems that turned out to be due to dirty, damaged, or worn-out equipment that was fixed or replaced once the right person had been notified.

This may seem surprising, but some of the best problem solving that I have seen has been done by competitors working together. I recall one case where three paint suppliers cooperated on root cause analysis and ended up dictating sections of the final report to the customer's paint people. All of us wanted to get the problem solved and get out of there... and back to improving our paints and developing new ones. We also wanted to avoid the wrath of a plant manager who seemed to be 7-feet tall, 300 pounds, and growing, especially when he was angry.

CONCLUSIONS

Surface defects hurt both appearance and the ability of a coating to provide protection. Some of the most common defects are cratering and other surface tension driven defects, dirt, popping and other volatile related defects, and flow defects. It is very important to prevent or cure such problems. The first step is to identify the defect which is not always straightforward. After that it is necessary to determine the root cause which usually takes a considerable amount of detective and analytical work. The most useful tool for diagnosis is the light microscope. Depending on the defect and the root cause, one or more countermeasures may be necessary, and these (and the results from them) should be documented for future reference. Cleanliness in the paint plant, during handling and transportation, and in the customer's factory are essential to the prevention of many defects.

ACKNOWLEDGMENTS

I would like to thank Beth Furar for excellent experimental results and photographs and William Brunat, Peter Kamarchik, and Keith Rowe for reviewing the manuscript as well as for many stimulating discussions.

References

(1) Pierce, P.E. and Schoff, C.K., "Coating Film Defects," 2nd Edition, *Federation Series on Coatings Technology*, Blue Bell, PA, 1994 (1st Edition 1988).

(2) Balch, T.C. and Seeman, R.W., *Soc. Automotive Eng.*, Paper No. 910095, SAE, Warrendale, PA, 1991.

(3) Fink-Jensen, P., *Farg och Lack*, 8, 5-14, 39-49(1962); *Farbe Lack*, 68, 155 (1962).

(4) Hahn, R.J., "Cratering and Related Phenomena," Journal of Paint Technology, *43*, No. 562, 58 (1971).

(5) Hansen, C.M. and Pierce, P.E., *Ind. Eng. Chem., Prod. Res. Develop.*, 12, 67 (1973).

(6) Bierwagen, G., *Progr. Org. Coat.*, 3, 101 (1975).

(7) Kornum, L.O. and Raaschou Nielsen, H.K., *Progr. Org. Coat.*, 8, 275 (1980).

(8) Schoff, C.K. and Pierce, P.E., *Organic Coatings Science and Technology*, G.D. Parfitt and A.V. Patsis (Eds.), Vol. 7, p. 173, Marcel Dekker, New York, 1984.

(9) Veneri, T.J. and Kramer, J.A., "A New Sample Preparation Technique for the Examination and Analysis of Paint Films Defect," Journal of Coatings Technology, *66*, No. 829, 23 (1994).

(10) Zisman, W.A., "Surface Energetics of Wetting, Spreading, and Adhesion," Journal of Paint Technology, *44*, No. 564, 41 (1972).

(11) Schoff, C.K., *Proceedings Electrocoat 92*, p.10-1, March 16-18, 1992, Cincinnati, OH.

(12) Schoff, C.K. and Chen, H.-J., *J. Oil & Colour Chemists' Assoc.*, 68, 185 (1985).

(13) Smith, R.E. and Boyd, D.W., "Electric Discharges During Ekectrodeposition of Organic Coatings," Journal of Coatings Technology, *60*, No. 756, 77 (1988).

(14) Schoff, C.K., *Proc. FATIPEC XX*, p.53, Nice, September 1990; "Electropaint—Substrate Interactions," Journal of Coatings Technology, *62*, No. 789, 115 (1990).

(15) Lockwood, K.A. and Wickham, S.R., *Mod. Paint Coat.*, 80 (7), 36 (1988).

(16) Brech, K.H. and Salman, S., *Proc. IBEC '97—Auto Body Painting*, p.121, Stuttgart, Germany, 1997.

(17) Zisman, W.A., in *Contact Angle, Wettability, and Adhesion* (R.F. Gould, ed.), Adv. Chem. Ser., No.43, Am. Chem. Soc., Washington, D.C. (1964).

(18) Good, R.J., *J. Adhesion Sci. Technol.*, 6, 1269 (1992).

(19) Schoff, C.K., *Wettability Phenomena and Coatings* in *Modern Approaches to Wettability: Theory and Applications*, p.375, M.E. Schrader and G. Loeb (Eds.), Plenum Press, New York, 1992.

(20) Hansen, C.M., "Surface Dewetting and Coatings Performance," JOURNAL OF PAINT TECHNOLOGY, *44*, No. 570, 57 (1972).

(21) Diversified Enterprises, 91 Main Street, Claremont, NH 03743; 800-833-4644.

(22) Owens, D.K. and Wendt, R.D., *J. Appl. Polymer Sci.*, 13,1741 (1969).

(23) Kaelble, D.H., *J. Adhesion,* 2, 66 (1970).

(24) Imai, T., in *Organic Coatings Science and Technology,* G.D. Parfitt and A.V. Patsis (Eds.), Vol. 6, p. 301, Marcel Dekker, New York, 1984.

(25) Panzer, J., *J. Colloid Interface Sci.*, 44, 141 (1973).

(26) Hansen, C.M., "Characterization of Surfaces by Spreading Liquids," JOURNAL OF PAINT TECHNOLOGY, *42*, No. 550, 660 (1970).

(27) C.M. Hansen and E. Wallstrom, *J. Adhesion,* 15, 275 (1983).

(28) Hildebrand, J.H. and Scott, R.L., *Solubilities of Non-Electrolytes*, 3rd ed., Reinhold, New York, 1950.

(29) Gardon, J.C., *J.Phys. Chem.* 67, 1935 (1967).

(30) Lee, L.H., "Relationships Between Solubility Parameters and Surface Tensions of Liquids," JOURNAL OF PAINT TECHNOLOGY, *42*, No. 545, 365 (1970).

(31) Beerbower, A., *J. Colloid Interface Sci.*, 35, 126 (1971).

(32) Barton, A.F.M., *J. Adhesion,* 14, 33 (1982).

(33) Barton, A.F.M., *CRC Handbook of Solubility Parameters and Other Cohesion Parameters,* p.415, CRC Press, Boca Raton, FL, 1983,.

(34) Osterhold, M. and Armbruster, K., *Proc. FATIPEC XXIV*, Interlaken, 8-11 June 1998, Vol.A, p.37.

(35) van Oss, C.J., Chaudhury, M.K., and Good, R.J., *Chem. Rev.*, 88, 927 (1988).

(36) Skrovanek, D.J., "Fourier Transform Infrared Spectroscopic Studies of Coatings Defects," JOURNAL OF COATINGS TECHNOLOGY, *61*, No. 769, 31 (1989).

(37) Watts, J.F., *Vacuum,* 45, 653 (1994).

(38) Briggs, D. and Seah, M.P., *Practical Surface Analysis*, *Vol.1 : Auger and X-Ray Photoelectron Spectroscopy*, John Wiley & Sons, New York, 1990.

(39) Duc, T.M., *Surface Review and Letters*, 2, 833 (1995).

(40) Briggs, D. and Seah, M.P., *Practical Surface Analysis, Vol.2: Ion and Neutral Spectroscopy*, John Wiley & Sons, New York, 1992.

(41) Benninghoven, A., *Angew. Chem. Int. Ed. Engl.*, 33,1023 (1994).

(42) Schoff, C.K., "Rheology," *Federation Series on Coatings Technology*, pp. 23, 38, Blue Bell, PA, 1991.

(43) Schoff, C.K., *Proc. 5th Annual ESD Advanced Coatings Conference & Exposition*, November 7-9, 1995, Dearborn, MI, p.77.

(44) Smith, N.T. and Shepard, D.D., *Eur. Coat. J.* 1995, 930 (1995).

(45) Shepard, D.D., "Studying the Drying and Curing Rates of Acrylic Automotive Topcoats Using Dielectric Analysis," JOURNAL OF COATINGS TECHNOLOGY, *68*, No. 857, 99 (1996).

(46) Schultz, J.W. and Chartoff, R.P., "Dielectric and Thermal Analysis of the Film Formation of a Polymer," JOURNAL OF COATINGS TECHNOLOGY, *68*, No. 861, 97 (1996).

(47) Schnall, M.J., "Flow Agents for High Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, *63*, No. 792, 103 (1991).

(48) Hajas, J., Bubat, A., and Dawid, B., *Farbe Lack,* 101, 675 (1995).

(49) Schwartz, J., Moyer, B.A., and Smith, R.E., "Control of Film Defects in Solventborne High-Solids Coatings: The Non-Additives vs. a New Additives Approach," JOURNAL OF COATINGS TECHNOLOGY, *70*, No. 884, 71 (1998).

(50) Blank, W.J., Berndlmaier, R., and Miller, D., *Paint Coat. Ind.,* 14 (10), 90 (1998).