Roger Dietrich

PAINT ANALYSIS

2nd Revised Edition

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Paint Analysis

The Handbook for Study and Practice

2nd Revised Edition

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Foreword

I am really glad that you found this book and opened it, curious to find out what to expect. This is the second edition of the book which was first published in 2009 and I can promise a lot of new interesting insights into field analysis and laboratory work with respect to coatings. Compared to the first edition you will find new techniques, additional advanced preparation and sampling methods and a lot of more practical examples. My intention was and is to share my experiences that I have made over the last 30 years in our laboratory and in the field with respect to the analysis of paints and coatings. I am a chemist and my approach to characterize a coating material, a raw material and coating failures is therefore primarily scientifically evidence based. I believe that is very important to have a profound insight into the basic, physical conditions and limitations of the analytical methods in order to comprehend their power and limitations. But I also have worked in the coating industry and know that is not always possible to investigate a problem extensively according to scientific rules. Therefore, I have tried in this second edition to shift the focus more to practical implications of analysing paints and coatings without neglecting the physical and methodical background. I added a section about sampling methods and representativeness because I have made the experience that the implications of proper sampling on the investigation result are too often disregarded.

Of course, you know the routine measuring and testing methods that tell something about colour, gloss and other physical conditions of paint films and coating material. These techniques provide the information **how** a certain material behaves. But they fail when it comes to the question **why** a tested material exhibits a particular property.

This is where this book comes in. I present a toolbox of analytical methods which exist for decades but have not yet found widespread use in the coating industry. However, I would like to demonstrate that the potential of the featured methods is incredibly big and far from being exploited.

The possible applications of the methods described here grow with the requirements of the samples to be examined. Almost every month a new question arises which can be answered with a process development based on the methods presented in this book.

Although I cannot deny my education as a chemist, the book is aimed at a broad group of users from the coatings industry. It is intended as an aid for the application engineer on site to start solving problems, but as well to provide the laboratory manager with suggestions for new ways of dealing with his tasks. I tried to build a bridge between the scientific view on the reality and the practical requirements on the site and in the applications laboratories.

I would like you to hold this book in your hands as a daily reference and tool, and to use it extensively to find out how you can

– reveal the causes of coating defects,
– investigate paint raw materials with respect to contaminations
– or analyse lacquered products in terms of their properties

So, if after a short time this manual is lying on your desk or laboratory table with paint stains and marginal notes, I would be more satisfied. In the practical part of the manual I have, therefore, tried to structure and process the topics in such a way that you can draw immediate suggestions for action if, for example, paint craters occur when coating products or if you want to know whether and how two paint batches differ. Of course, this is backed up with theoretical principles in a separate chapter. But the problem solutions described in the practical part should ideally enable you, like a kind of “recipe”, to proceed directly to action with the book in your hand to tackle your daily challenges.

I do not see this book only as a handbook documenting the current state of the art, but I would like to use it to stimulate dialogues from which improvements of current procedures or perhaps even new developments can arise. I am therefore always open to suggestions and comments and hope to receive numerous feedbacks, which I will gladly take up and answer as soon as possible.

Münster, November 2020

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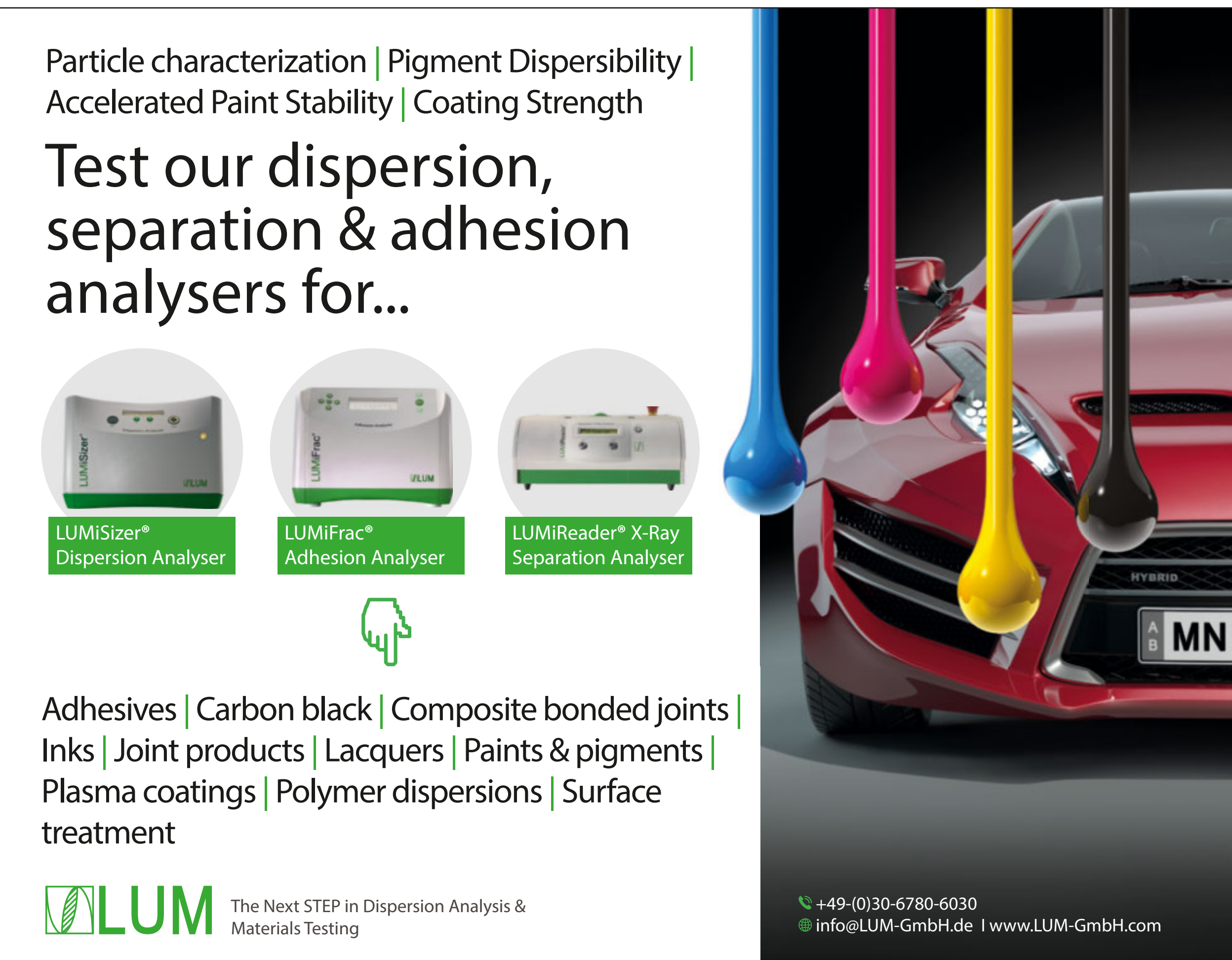

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Part I General information about paint analysis

For the investigation of paints, semi-finished products, raw materials and finished coatings, a very extensive "toolbox" of the most diverse analytical methods is available today. This is sometimes a bit confusing for the non-analyst. For an effective use of the individual methods, it is necessary to have a very detailed knowledge of the possibilities and limitations of each method, the excitation modes and the information to be expected. The book that you just opened will try to shed some light on the thicket of methods. A great deal of attention is given to surface processes, as the majority of questions arising in practice are related to surface phenomena in one way or another. But also the so-called "bulk analysis" plays an important role in this book. Classical test methods such as climate-testing, solar simulation etc. are deliberately omitted because these are test methods for a certain parameter but have a completely different objective and are not analysis techniques.

1 The surface

This book deals with the application of modern techniques to paint analysis, with a special focus on surface analysis. If one thinks about the word "surface", it quickly becomes clear what a relative and vague term it is. To a painter "surface" does not mean the same as it does to a surface chemist. To a painter, the surface represents that part of an object which is usually presented to the outside world and can be touched and observed directly, see Figure I.1. A painter considers a brushed

Figure I.1: Solvent droplets on a brushed, hydrophobic steel surface

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visually clean steel surface. However, it can also be defined as the boundary layer between a solid or liquid material and a surrounding liquid or gaseous phase.

A surface physicist would probably refer to it as a phase interface. Alternatively, it could be defined as the area of a solid or liquid thing at which the bulk physical and chemical properties change instantly, a so-called property boundary.

A surface chemist, however, is talking about the uppermost molecular layers of a material when he uses the word surface. This is an area that cannot be observed without the help of analytical techniques. In fact, the uppermost layers of an object often determine the quality and behaviour of the material as far as (paint) adhesion is concerned. The uppermost layer of the steel surface is not directly visible without the help of machines. Probably the steel surface exhibits a chemical surface modification which explains the hydrophobic behaviour visible in Figure I.1. Or there is a thin layer of contaminations that produces a hydrophobic property!? – To define this is the task of surface analysis.

Definition of the term surface

So, let's first define how to use the word surface in this book. **A surface is a boundary layer which separates a substrate from the surrounding environment (air, liquid). It is typically 1 nm to 1 μm thick.** In contrast, a "thin layer" is defined as being 1 μm to 10 μm thick.

The surface plays a significant role in the physical and chemical properties of a material. A contract painter, for example, who paints and coats coils and metal profiles has to rely on the surface quality of the goods he is going to coat. The surface of the raw material that he receives might well look clean. However, the material has a long history before it has been delivered to this company to be painted or coated. During production, storage and transport of a coil, for example, numerous substances may have been adsorbed onto the surface. This surface layer contaminants may not be visible, but it always exists! And sometimes even traces of contaminants can seriously impair the adhesion of a coating to a surface.

When it comes to processing of the coil, the chemical composition of the outermost molecular layer plays a significant role. If the coil has been coated with a protective layer of oils to prevent

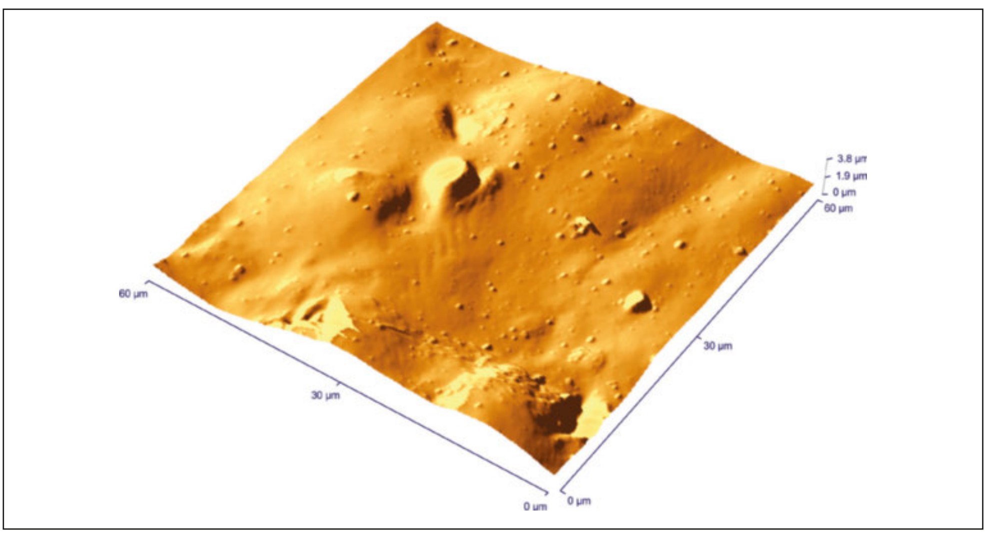

Figure I.2: AFM (atomic force microscope) image of a paint surface (60x60 μm) corrosion during transport and storage, the paint will exhibit poor adhesion or craters after application. Even a monomolecular layer of some of these oils can have deleterious effects on coating procedures.

As these ultra-thin layers are invisible, the unfortunate manufacturer is in fact "blind" as far as the surface quality of his coils is concerned. In most cases, therefore, he will decide to install a cleaning process before applying the coating. But he will do so without knowing if it is necessary and, even worse, without knowing what to remove from the surface. Unfortunately, there is no "magic" process for eliminating all the various kinds of contaminants. His efforts might well produce a surface quality worse than before, due to the presence of oil residues and traces of cleaning chemicals, such as surfactants.

Some goods require a pretreatment like e.g. phosphating before coated. The quality of the deposited anti-corrosion phosphate conversion layer is significantly depending on the parameters of the process. Only well crystallized zinc or iron phosphate guarantees a perfect adhesion of the subsequently applied coating. Without analytical methods like e.g. SEM or infrared external reflection spectroscopy, it is impossible to check the performance of the pretreatment process with respect to crystal morphology and percentage of coverage. The author has worked on a lot of adhesion failures issues during the last twenty years which have been caused by poor conversion layer application, although on impulse the painter has been blamed.

Another focus is on the coating material itself. As the paint and the painted substrate have to be a chemical match if good adhesion is to be obtained, a few questions need to be asked before the painting process is started.

- What is the chemical composition of the substrate surface?
- Which pretreatment can be used to improve paint adhesion and what effect will it have?
- How do the paint ingredients influence the surface of the material that has to be painted?
- What influence do the paint additives have on paint adhesion?

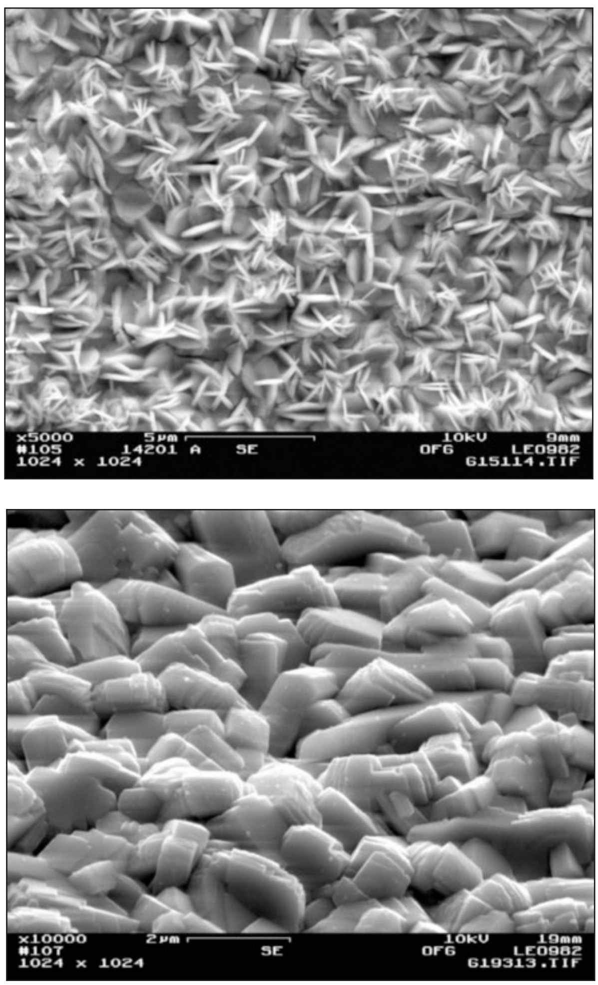

Figure I.3: SEM Images of different zinc phosphate conversion layer morphology

Unfortunately, these questions often can't be answered by simple tests or classical chemical analysis, because they require an ability to analyse tiny amounts of substances that have high **surface sensitivity**. Only the surface analysis techniques described in this book can answer these questions

A growing field of application for modern surface analytical techniques is not only paint application but also paint production. Modern high-performance paints have to fulfil many requirements simultaneously that are sometimes hard to match. This does not only create a demand for characterisation of the raw materials and products. The chemical interaction of paint compounds and the reaction between each compound and the ingredients of the substrate (e.g. a polymer) are also key parameters.

If, for example, a moulded polymer part has to be coated, it is not just the polymer which is of interest. The manufacturer or supplier of the raw material compounds the polymer to customer demands. In accordance with the requirements imposed on the polymer material, he adds additives to improve flame, light, impact or heat resistance. One parameter the supplier is not concerned about is the paintability of the product made from the granules which he supplies. That is a process which the polymer supplier does not see.

However, it has been shown in the past that additives present in polymers "designed" to enhance moulding processes, e.g. offering for example good release from injection moulds, exhibit poor properties with respect to surface finishing by painting. Most of the additives incorporated into a polymer migrate to the surface, driven by temperature, humidity, time or solvents. This sometimes leads to unpredictable results, such as paint adhesion failure, chemical reactions, discolouration, and wetting failure. Many manufacturers of paint for automotive interior parts have therefore discovered, that it is essential not only to know their own paint manufacturing process, but also to learn something about the polymers which have to be painted. This is a task that can easily be fulfilled by the techniques which are described in this book.

2 Why paint analysis?

A few years ago, the author was talking to the CEO of a paint manufacturer who had different issues with costumers complaining about the performance of several paint types on a constant level. I asked him if he ever thought about using the powerful toolbox of analytical methods to improve his paint production. He answered: "We sell lacquer, we are not an analytical company!"

For him "selling" was the key word. For the quality of the incoming raw material he relied on the factory test certificate of the suppliers, with respect to the quality of the produced paint he banked on his processes.

But certificates provided by the supplier do not tell everything, what is essential to know to ensure a safe and high quality production. The best process documentation and compliance cannot guarantee a flawless production. In addition to that, the experience has shown that a lot of customer complaints in the field are not substantiated, because they based on application faults in the coating process. Without knowledge about the details of raw materials, the products and the field application a manufacturer is on a constant "blind flight". Some paint producers have understood this and profit from a well-equipped laboratory and excellently educated lab staff. But for the commercial department a laboratory and analytical operations are very often simply "lost" costs without profit. On the long run however it pays off to understand the details of a production line. It is a competitive advantage to understand the details of a costumer`s paint shop to avoid unsubstantiated complaints and help him to improve his process. And it is good to know the raw materials in detail to save costs with respect to production failures caused by deficient raw material.

Often, when assigning an investigation task to an internal or external laboratory, high expectations are placed on the laboratory:
- It should be done quickly ("Best by the day before yesterday")
- There must be no charge
- One analysis should, if possible, comprehensively solve the entire possibly complex production problem

It should not be surprising, that these wishes will not come true. Solving a production problem normally requires complex procedures, with analytical methods providing the necessary facts. But this process avoids expensive "try and error" actions and aimless activities. The prerequisite for a reliable solution based on measured data are:
- A qualified problem analysis
- caution during sampling
- the selection of appropriate testing methods
- specialist knowledge of the laboratory
- experience in the evaluation of measurement data
- accuracy in the interpretation and formulation of results
- sound translation of the results into the process

This requires a very intensive exchange with the laboratory in order to effectively combine in-house knowledge and process know-how with the knowledge generated by the analysis. The dividing line between the internal knowledge of the commissioning company and the external knowledge of the laboratory depends on the personnel structure of the company. A contract coater with a more artisan orientation will usually not know and need many details about paint chemistry, while an automotive supplier specializing in industrial series coating often has its own competence teams on site for all questions of paint chemistry. Both they can also benefit from instrumental analysis methods if these are used in the service and, if necessary, the knowledge of the laboratory service provider is taken into account. Roughly speaking, the less knowledge about the processes and materials in the commissioning company, the more the external knowledge of the service provider can and should be consulted. If this interaction works well and smoothly, in some cases even one analysis costing a few hundred Euro, can save five times as many costs for complaints or faulty batches.

3 Relevance of modern analytical techniques to paint analysis

There are hundreds of techniques for analysing paints and coatings. They yield information about viscosity, gloss, haze, hardness, acid value, etc. In other words, they describe the product and its properties. They ensure that the desired level of quality is achieved. On the other hand, standard analytical tools often fall short when failures and production problems arise. The standard techniques are perfect for checking the quality of a product. However, if a product is defective and the root cause has to be investigated, the standard techniques are not very helpful. For example, a monomolecular layer of a release agent on the surface can easily cause severe adhesion failure if