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THE USE OF ELECTRON MICROSCOPIC METHODS FOR THE CHARACTERIZATION OF PAINTS IN FORENSIC SCIENCE

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Abstract

Apart from the conventional methods for investigating paints in the forensic science laboratory the electron microscope gives many additional types of information. Since the materials for coating objects are produced in large quantities, a merely chemical analysis of paint does not lead to individual identification. Therefore it is necessary to demonstrate morphological peculiarities, such as e.g., features and defects of fabrication. So the material will have to be evaluated by microanalysis and cathodoluminescence, too. Additionally the pigments and extending materials, especially in primers, can be described by transmission electron microscopy. In that way one can obtain information about the distribution of grain size or the form of single pigment particles. The application of the transmission electron microscope is of special interest to the field of the new pearl lustre pigments.

KEY WORDS: Scanning electron microscopy, transmission electron microscopy, paint, pigments, pearl lustre pigments, cathodoluminescence, traffic accidents, forensic science.

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Introduction

Paint occupies an outstanding place among the numerous materials that have to be analyzed by a forensic scientist in his daily work. Many objects of everyday use are coated with paint. Thus it cannot be avoided, that these coatings leave their marks, whenever heavy forces have acted on them. In many cases it is possible to deduce from these traces clues to the offender or to the way the crime happened. This could for instance be of impact on the elucidation of traffic accidents or as evidence to the question of whether or not a certain tool was used to open a door or a safe.

Great difficulties in characterizing the material "paint" as comprehensively as possible in the forensic laboratory are caused by two factors. Firstly, paints are normally produced and used in huge quantities. For that reason an individual assignment only through the analysis of the material will hardly be possible. Therefore, the features of processing have to be investigated extensively, too, e.g., the structure of the particular layers. Secondly, the scientist has to deal with very small amounts of material in most cases, and the form of the particles may often have altered. Therefore it is necessary to use many different methods for analysis in the forensic laboratory to register all features as comprehensively as possible (Ryland and Kopec, 1979).

Materials and Methods

The scanning electron microscopy (SEM) with its different facilities of examination is one of the most useful modern methods in a well-equipped forensic laboratory. For many years we have also been using transmission electron microscopy (TEM) in addition to the SEM. Thus we have the possibility to evaluate the micromorphology and the chemical composition of single particles of pigments and extending materials.

The following examinations were made by use of a SEM CamScan Model S4 with Electron Beam Microanalysis System Kevex 8000 and by a TEM Hitachi H 500 with analysis system Kevex 5100. For SEM the specimens were prepared by carbon coating in a Leybold coating equipment EPA 100. The preparation for TEM will be described below.

The cross sections have been produced in a way similar to the one described by Ward and Carlson, 1983.

Scanning Electron Microscopy

In the examination of paint samples the SEM is mostly used as a first complementation of the light-optical microscope to provide for better evaluation of morphological features. For example, one can produce a cross section which will make the single layers much better visible than the light microscopy. In secondary electron (SE) images the structures can be more clearly visualized due to the completely different mechanism of image formation (Figs. 1a and 1b).

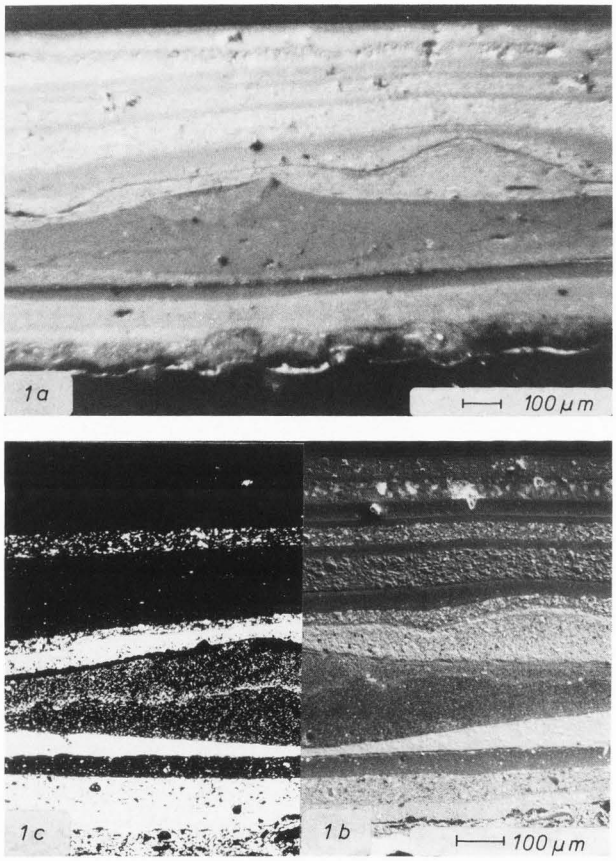


Fig. 1: Cross section of a fragment of household paint (18 layers)
1a: Light-optical microscope
1b: BSE image in SEM
1c: SE image in SEM

In addition to this we now have the possibility to obtain analytical information from the depicted surface area. The backscattered electron (BSE) image, obtained e.g., by the use of a solid state ring detector also provides information about the composition of the material (Fig. 1c) and serves mainly as a basis for subsequent elemental analysis with the energy dispersive X-ray analysis system (Nolan & Keeley, 1979; Gardiner, personal commun.). In some cases, one can abstain from the time-consuming X-ray mapping pictures, if the BSE detector has a satisfactory energy resolution ($\Delta Z<2$). In these cases a "spot-analysis" is sufficient for an analytical characterization of the single layers. However, sometimes it is necessary, especially with inhomogeneously structured layers, to produce X-ray maps of some elements (Figs. 1d - 1f). On the other hand, the "line-scan" configuration mostly does not provide any additional and important information with materials of this type.

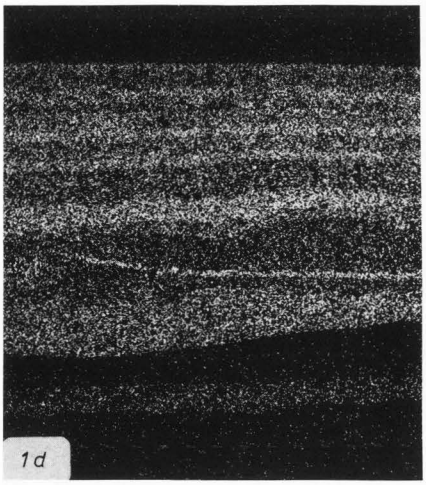
In many paint materials it is meaningful to test also the luminescence features of each component in addition to the chemical analysis. Fig. 1g shows cathodoluminescence (CL) in the zinc-containing layer, but also partly in the layers showing an accumulation of the element calcium. One can clearly see that for example the calcium-containing layer consists of material of different composition (with and without luminescence).

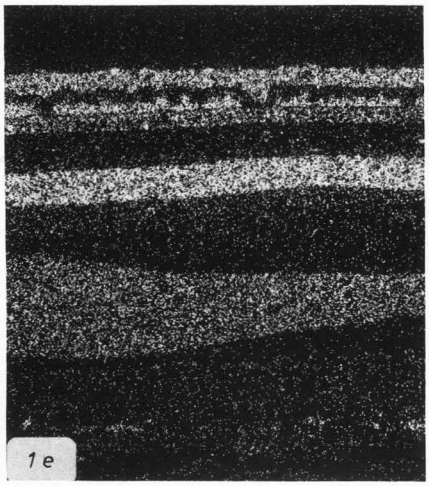
The test of cathodoluminescence is important especially with titanium dioxide-pigmented paints, because we are able to tell apart the modifications rutile and anatase by this way: anatase shows cathodoluminescence, rutile does not. It is well known, that there are no possibilities to differentiate between these two modifications of TiO_2 by any usual analytical methods, except by X-ray diffraction (Curry et al., 1982).

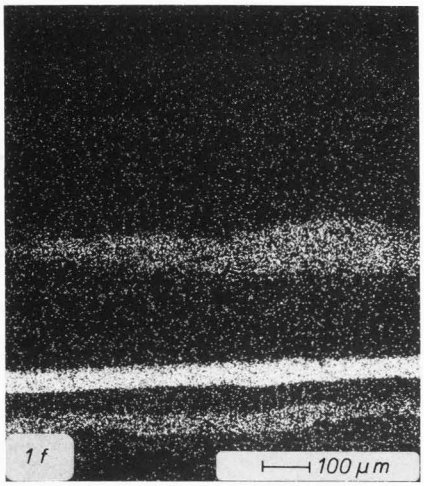
Compilation of all these results provides a very good material characterization of the paint fragment. In the usual comparison evaluations in this way mostly a meaningful expert opinion can be stated on whether two objects correspond or not. Furthermore, these results can be supplemented by photographing the cross section of paint in a light-optical cathodoluminescence device. Here the different colors of the luminescence show some additional and important features (Fig. 1h) (Goebel and Patzelt, 1976; Stoecklein and Goebel, 1984). The excitation of the cathodoluminescence is performed in this equipment by a powerful electron beam in a Leitz contrasting unit. In this process the single layers are etched and eroded by the electron beam depending on composition of the material. Therefore, observation and taking pictures should last only a few minutes. Afterwards the cross section may be polished easily.

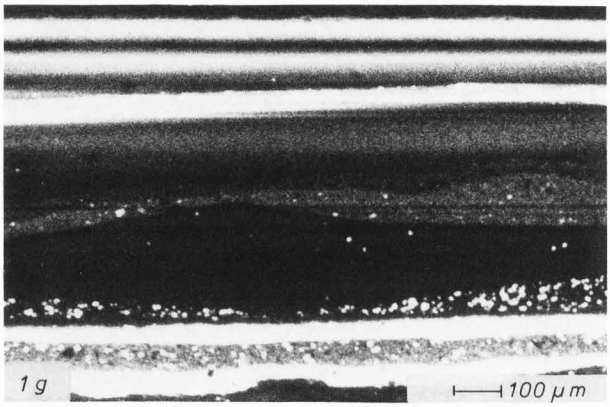
In paint comparison evaluation of car lacquers it may be worthwhile if the scientist succeeds in finding individual marks on the material tested which correspond to certain events in the life history of the vehicle, e.g., to repair work. Figs. 2a - 2c contain a cross section of a one coat metallic car paint, consisting of a silicon-containing primer and a transparent topcoat with aluminum chips inside. On the surface of the lacquer one can see an additional, very thin layer containing silicon. This may be due to a car polish. This feature is not identifiable in the light-optical microscope nor by any material analysis. It certainly can be regarded as an individual characteristic.

For some time, a few types of cars have been produced with a totally zinc galvanized body before paints were applied to prevent corrosion (Porsche, Audi). When we have to test paint frag-









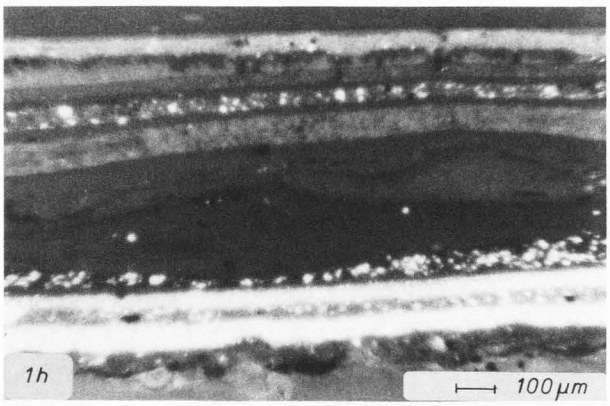
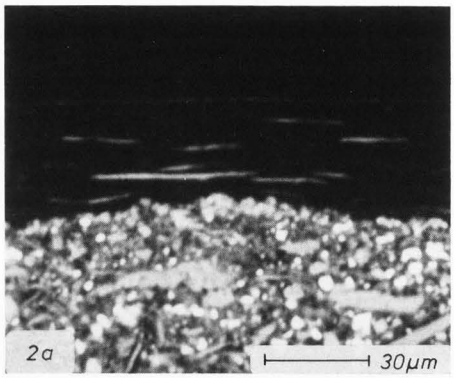
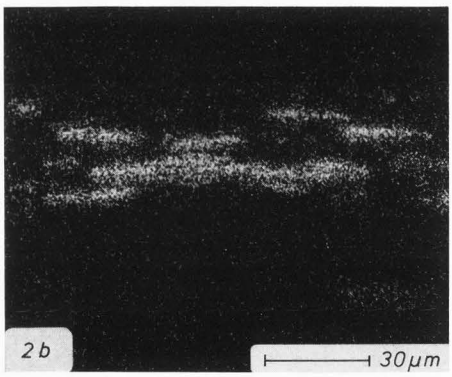


Fig. 1d: X-ray mapping barium/titanium
1e: X-ray mapping calcium
1f: X-ray mapping zinc
1g: Cathodoluminescence in SEM
1h: Cathodoluminescence in light-optical device





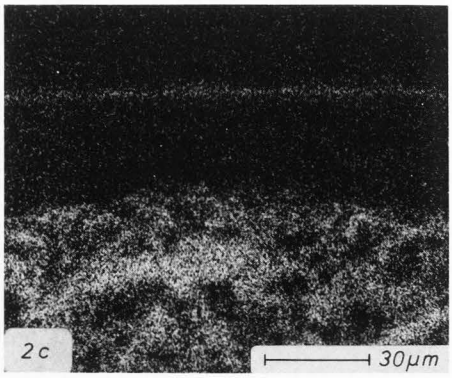
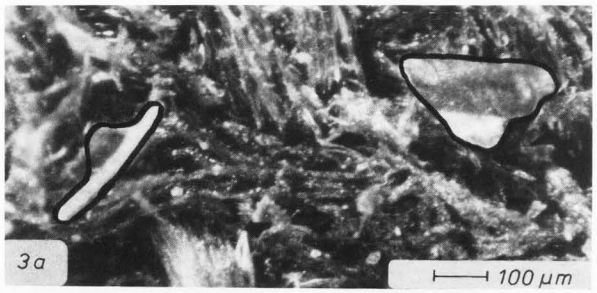


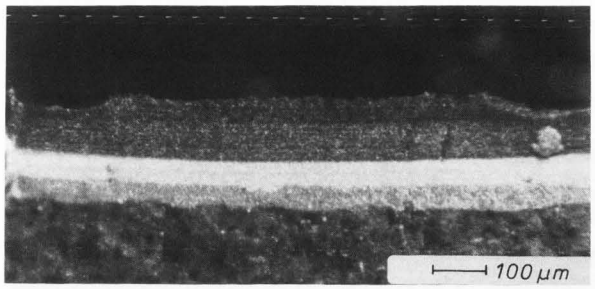
Fig. 2: Cross section of a two-coat metallic car paint flake
2a: SE image
2b: X-ray mapping aluminum
2c: X-ray mapping silicon

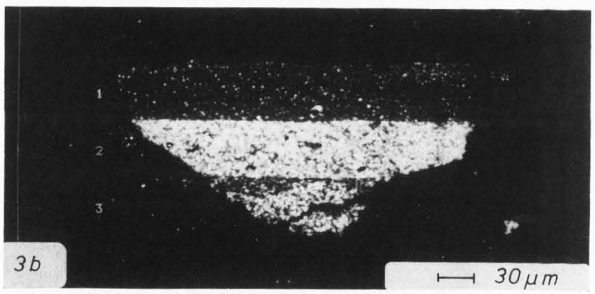
ments of such a car after an accident, we find very different composition of only zinc phosphate crystals on the undersurface of the primer in contrast to the usual zinc phosphate combined with iron-containing crystals from the "normal" production method. Such information is important mainly in cases, where paint flakes have been found at the site of an accident or even of the scene of crime and when the question arises, which type of car was involved in the event. In addition to the evaluation of the color by microspectrophotometry and of material by various analytical methods, the result of SEM examination described above may also contribute to the identification of the vehicle.

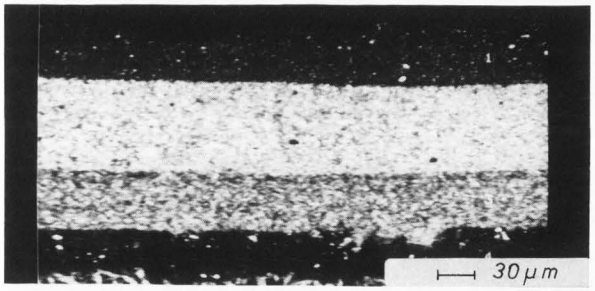
A great advantage of the scanning electron microscope is the possibility to analyze tiny grazed particles of paint directly on the carrier. Thus there is no danger of losing or altering the material during separation. One example is shown in the following case. A pedestrian was hit and killed by a car and the driver fled. In the laboratory we discovered on the coat of the pedestrian some very small red particles of paint under the binocular microscope. Small paint flakes were found on the street at the site of the accident as well. During the investigation policemen discovered a suspicious car and took some material for comparison purposes.

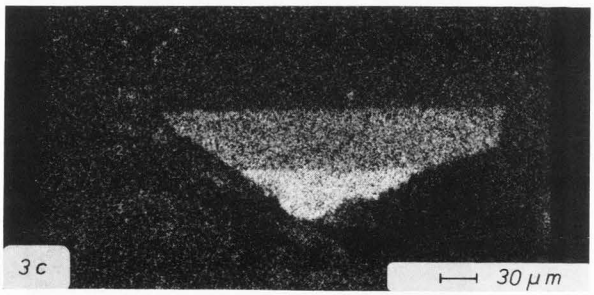
Small areas of the textile with attached particles of paint were cut out. Then these were carbon-coated and brought directly into the SEM. The comparison material had been cut at an angle, so that all layers were visible. Fig. 3 shows the particles from the clothes (3a) and from the car, the corresponding BSE micrographs in SEM (3b) and the elemental distribution of the elements barium (3c) and lead/sulfur (3d). The tests

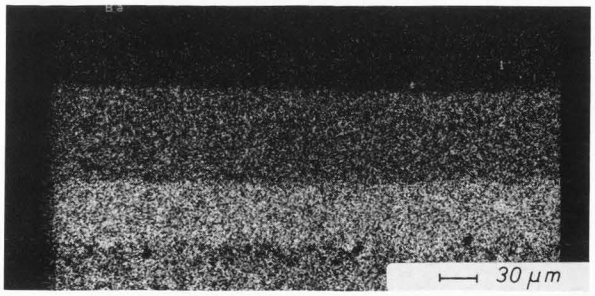


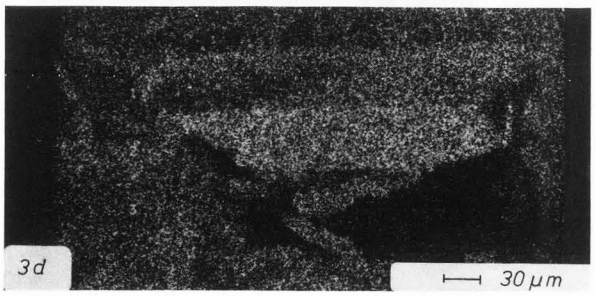


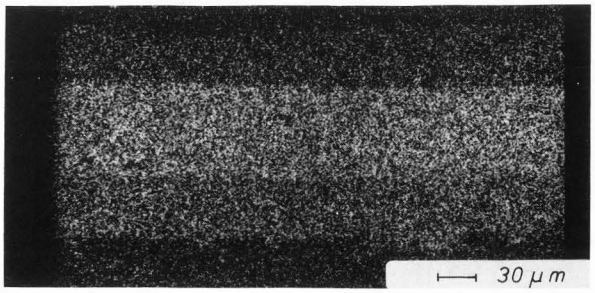










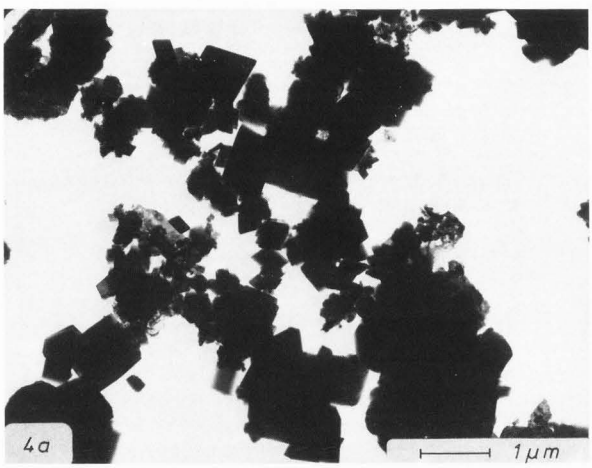


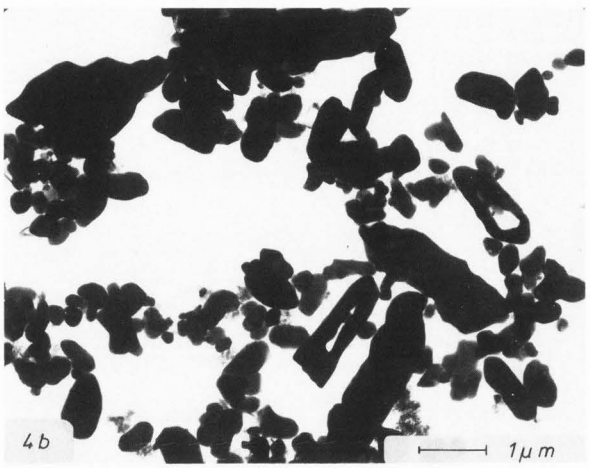
show that the paint particles compared consist of single layers with the same material compositions. Even if we cannot clearly demonstrate from this result, that the material is of identical origin, we can show, that it is possible to analyze these small quantities of evidential material in an extensive way. At least we can give important clues as to the connection of the suspected car to the accident. In cases with such small quantities of material only evaluation in the SEM could produce valuable results.

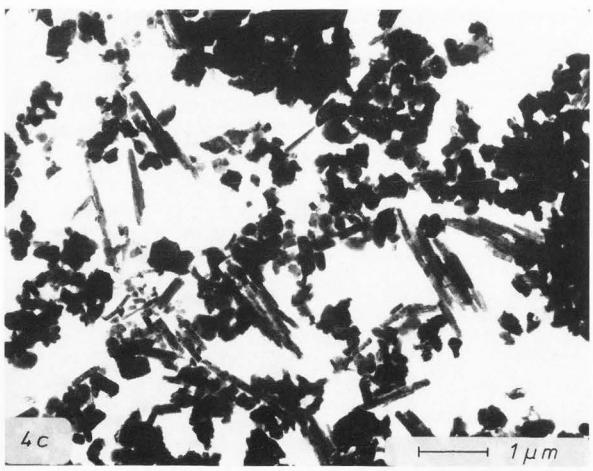
Transmission Electron Microscopy

We have also been trying for many years to obtain characteristical features of vehicle paints, and especially of primers and fillers by evaluating the micromorphology of the inorganic components. This is possible only in the TEM, because here the grain structures appear as silhouettes. Small particles of paint have to be ashed for preparation, dispersed in water by ultrasonic equipment and afterwards sedimented onto the specimen grid. The micrographs show a wide variety of grain structures, which are generally characteristic for the different manufacturers. Figures 4a - 4d show primers of four manufacturers. The structures are clearly varying. The elemental composition of each particle can be identified by EDX-analysis. The cubic crystals of 4a (Opel) for example contain the element calcium ($CaCO_3$). Interestingly enough the irregular shaped solid particles as well as the elongated open particles in 4b (Audi) consist of $BaSO_4$.

All the results of analyses of vehicle primers available today have been collected in an atlas. Through this work it is possible in many cases to identify the manufacturer of a certain car paint fragment after the evaluation of the primer material in TEM only. However, in order to build up a complete collection we shall need







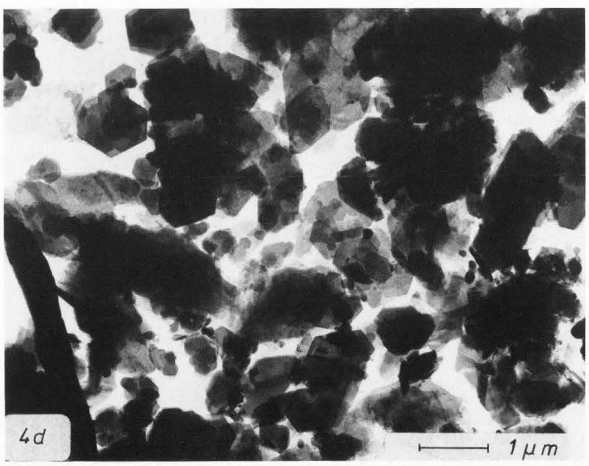


Fig. 3: Paint chips
left: on textiles; right: from the car
3a: Light-optical microscope
3b: BSE image
3c: X-ray mapping barium
3d: X-ray mapping lead/sulfur

Fig. 4: Transmission electron microscopic images of 4 different primers
4a: Opel 4b: Audi
4c: Karmann 4d: Mercedes

much more time. At first, it will be necessary to develop a suitable system for the classification of the micromorphological features.

A further significance of TEM investigation of paints will be shown in the application of pearl lustre pigments (Iriodin/Afflair). These pigments have been used in the USA in recent years and will be used more and more also in Europe for car coating. In contrast to the usual light-wavelength absorbent pigments the colors in these materials are produced by effects either of interference or of a combination of interference and absorption. Pearl-effect pigments consist of thin layers of highly transparent metal oxides with high refractive indices (e.g., titanium dioxide, rutile or anatase) on substrates with low refractive indices (mica). Also, a combination with thin layers of absorbing metal oxides like Fe_2O_3 or Cr_2O_3 is possible (Fig. 5). The color depends on the thickness of the layer (100 - 500nm) or on the combination of several layers. The intensity of the "pearl-effect" can be altered by varying the diameter of the substrate particles (5 - 150µm). (Dorfner, 1982; Esselborn, 1985; Esselborn et al., 1986).

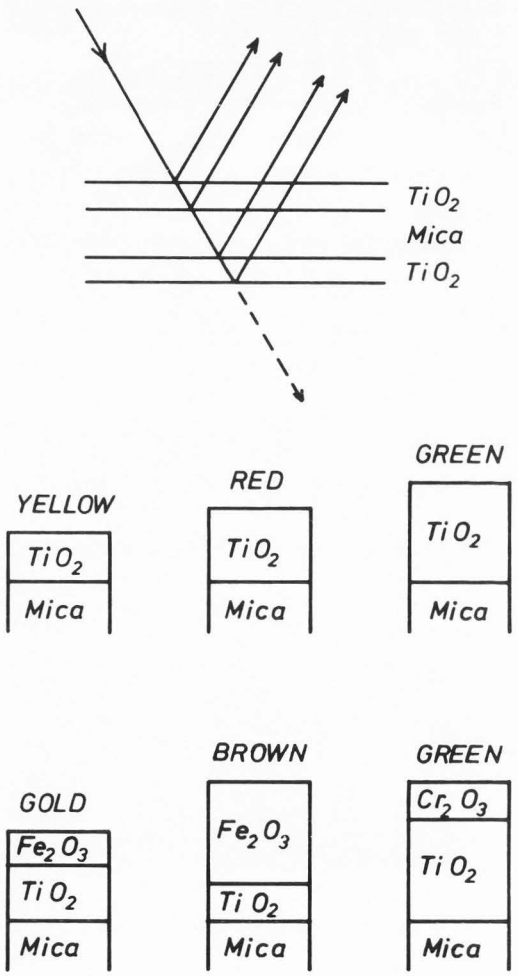


Fig. 5: Reflection of light and various compositions of pearl-lustre pigments

These pigments may be evaluated very well in the TEM, and in some cases this will be necessary. If these sorts of pigments would become more and more common - which seems quite probable - the forensic scientist will not only have to analyze the chemical elements and the phases (e.g., by X-ray diffraction) but also to check the particle morphology. When for example, the element titanium has been found, this might have been due to a normal TiO_2 pigment (grain size 0.3 - 0.8µm) or, alternatively, from a Iriodin/Afflair pigment with titanium dioxide coating. In the latter case, an electron diffraction analysis may be useful to identify the mineral mica (Muscovite). At any rate a certain degree of caution in the evaluation would be necessary in such problems.

Our experience until now has led to the opinion that a differentiation of the various manufacturers will be possible, in principle, by morphology and analysis, possibly in combination with X-ray or electron diffraction. Figures 6a - 6d show some pearl lustre pigments. The different structures can clearly be seen. The single particles have to be analyzed by EDX. In addition to this the transparent structures may be identified by electron diffraction. In Fig. 6d difficulties in manufacturing become evident: the substrate particles are torn to pieces. Coatings of such material do not show a good pearl-lustre effect.

Conclusion

In the testing of paints in the forensic science laboratory electron microscopy represents a useful and important complementation of conventional testing methods such as chemical analysis, emission or absorption spectrography and X-ray diffraction. In many cases, especially with very small quantities of material or with multilayered paint fragments the versatility of SEM evaluation leads to acceptable results. The still very rare use of TEM in forensic work can be of great advantage to a complete evaluation of solutions to special problems. However, it will be necessary to systematically build up a data file of materials which can be used for identification in particular cases.

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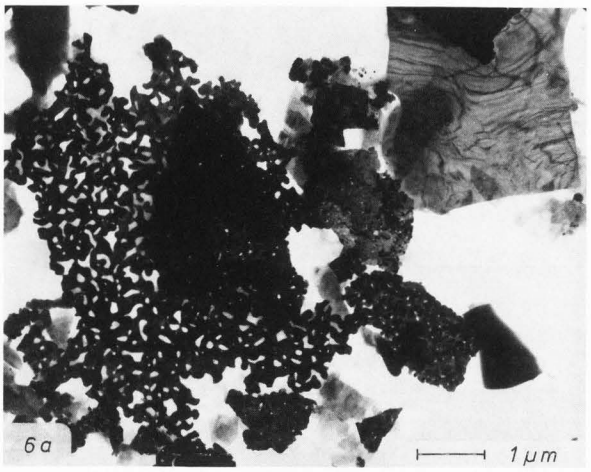

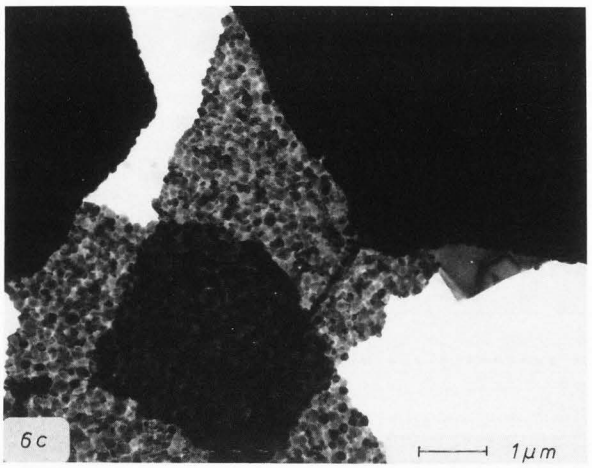

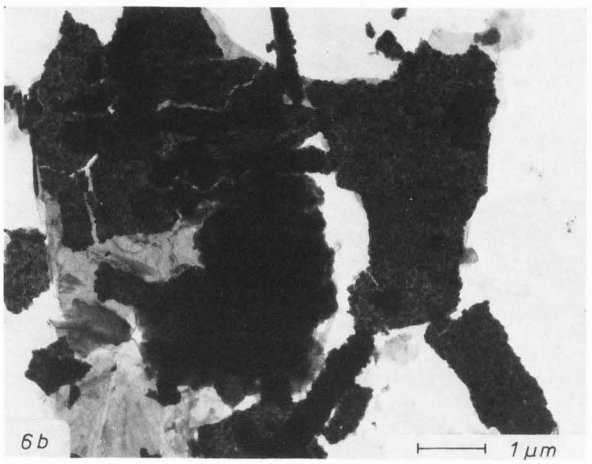

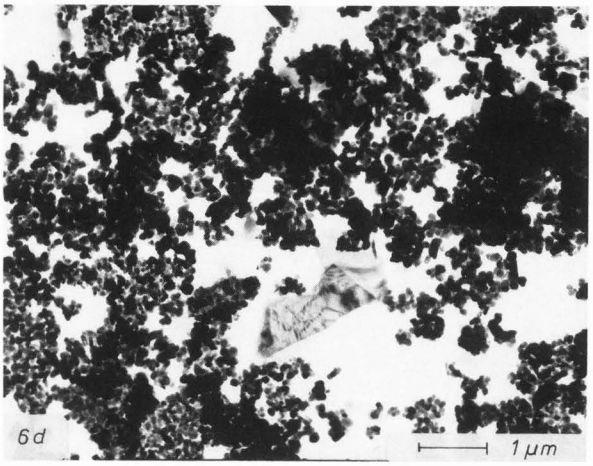

Fig. 6: Different pearl-lustre pigments
6a: reddish brown, main element Fe
6b: gold, main elements Fe, Cr
other elements Ti, Mn
6c: red, main element Fe
other elements Al, Si, Ti, K, Cr
6d: reddish brown, main elements Fe, Al, K
other elements Si, Ti

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Discussion with Reviewers

J.A. Brown: What can cathodoluminescence tell about the structure of matter? For example, why does rutile and anatase have different cathodoluminescence?

Authors: Cathodoluminescence of a solid depends essentially on the distance of its valence- and empty band. Direct transmission from charge carriers between the bands of typical insulators

(e.g., white pigments, extenders) are statistically improbable on account of the magnitude of distances (7-10eV). However, using centres of luminescence - e.g., trace activators or lattice imperfections in small concentrations (1:1000) - electrons which have excited from valence to empty bands by means of electron bombardment may return into the valence band via an "energetic bridge". The energy which is just generated is being emitted as a photon. Traps and quenching centres (e.g., iron ions) have an influence on the amount of luminescence.

In the analysis of coatings cathodoluminescence is an appropriate tool for the differentiation rather than identification of pigments and extenders, since identical minerals may exhibit different colors of luminescence if only they contain different trace activators. In a crystal lattice smaller distances of atoms (ions) lead to broadening of the bands and thus produce smaller band-edge distances. The probability for the formation and recombination of electron-hole pairs is thus increased.

From the three TiO_2-modifications rutile, anatase and brookite, anatase has the smallest distance of the titanium ions in its crystal lattice. The direct transmission from one band to another involving the emission of visible light is possible only with this modification in crystal structure, since with anatase cathodoluminescence is independent of the concentration of trace activators.

P.J. Nolan: How often do you detect anatase in modern paints? In our experience it is used very rarely.
Authors: It meets our experience that anatase is used very rarely in automotive top coats. However, we find this pigment very often in emulsion paints, in coatings of ships and in many primers and fillers.

S. Seta: How do you prepare the cross sections of paint samples?
Authors: We use to embedding our paint fragments in polyester (Castolit resin, Buehler Ltd.), grinding with SiC (grain size 600) and polishing with CeO with an automatical polishing device. We will shortly report on a new technique of preparation for cross sections and thin-cuttings using an ultra-milling-machine.

D.C. Ward: Would you elaborate on the sample preparation method for TEM, and what would you consider to be the minimum sample size required for this technique?
Authors: The paint particles are heated in a little porcelain boat so far, until the organic components are volatized. Afterwards the particles have to be dispersed in 0.5cm^3 water by means of an ultrasonic device. One droplet of the fluid will be set onto the film-coated specimen grid by aid of a capillary and allowed to dry. Paint fragments of less than 100 µg are easily analyzed by this method.

D.C. Ward: As most Forensic Science laboratories are not equipped with TEM do you feel that SEM could reveal sufficient grain structure to discriminate between primers if the sample is dispersed in a manner similar to what you describe?
P.J. Nolan: Is it possible to examine the morphology of pigment and extender particles using microtomed sections of paint in the TEM? What advantages does your method using the TEM offer in comparison with other techniques such as SEM or X-ray diffraction?
Authors: The evaluation of the grain structure of primers is much more difficult in SEM. Especially the fine structures of some components (as in Fig. 4c) cannot be shown in a quality as necessary to identify them. By use of the much better resolution of the TEM the possibilities of evaluation are improved compared with earlier experiments using scanning transmission mode in the SEM (Keeley RH, Robeson MC. (1975). The routine use of SEM and electron probe microanalysis in forensic science. Scanning Electron Microscopy 1975: 479-486). The evaluation of microtomed sections of paints in TEM will have only minor success, because the relatively hard particles will be put out of the surface during cutting. In that way one produces a lot of artefacts. If somebody wants to make an in-situ evaluation of the pigment grains it seems to be better to uncover the particles by ion etching or cold ashing and afterwards to use the replica technique with metal coating at an angle (Kaempf G, Liehr W, Voelz HG. (1970). Elektronenmikroskopische Untersuchungen an pigmentierten Lacken und Kunststoffen (Electron microscopic examinations of pigmented lacquers and resins). Farbe und Lack, Vol.76, No.11, 1105-1111). This method may be useful to evaluate the distribution of the pigments and other inorganic components in the layer, but, on the other hand, we can resolve this special problem by use of modern light-microscopical methods.

The examination of pearl lustre pigments in SEM provides only very rough information (Fig. 7). The EDX analysis of the thin single-layered or multilayered metal oxides in SEM is hardly possible because of physical restrictions.

The X-ray diffraction is an absolutely independent additional method, because it delivers information on the crystal structure in contrast to the elemental information of the EDX analysis. This method also cannot be replaced by electron diffraction in TEM, since many pigments (e.g., TiO_2 or $BaSO_4$) are not identifiable by electron diffraction due to the low penetration power of the beam. On the other hand one can purposefully analyze single electron-transparent particles (Mica, Sepiolite). Anyway, the X-ray diffraction is a method, which does not require a lot of time or manpower and so we have the opinion that it should be used whenever it is possible in paint examination routine work in addition to the techniques of electron microscopy.

P.J. Nolan: How do you assess the significance of the presence or absence of an apparent wax polish layer?
Authors: In case work we are essentially investigating smears, which normally do not exhibit undestroyed surfaces, which might be used to

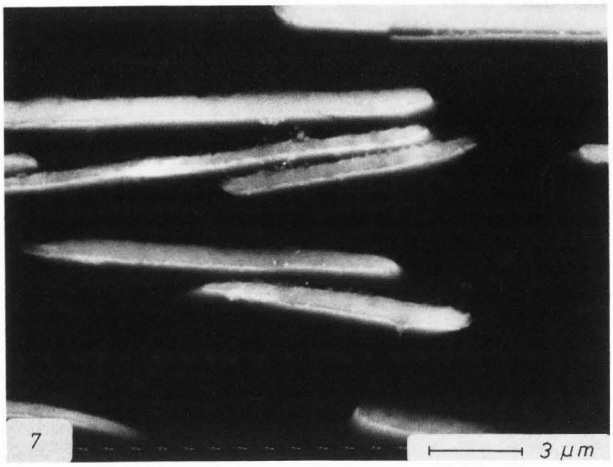

Fig. 7: BSE image in SEM of a cross section of a pearl lustre pigmented top coat

prove the existence of residues of waxes or polishing agents. In view of the relatively small number of cross sections which have hitherto been analyzed (ca. 100) a marked silicon-containing surface layer such as has been described in this paper has occurred only once.

S. Seta: What is the degree of variability of the grain structures of the car paint of the same color?
Authors: Apart from different components of binders identical colors of automotive paints from different paint producers normally also contain different compositions of pigments, which may be differentiated both morphologically and by elemental analysis using TEM - if they are inorganic.

P.J. Nolan: How many cases a year that involve paint does your laboratory examine and of that number what proportion are examined by SEM and TEM?
Authors: Following our experience we can show, that up to 150 cases a year are brought into our laboratory which involve paint examination. About 20% of them are analyzed in SEM. The number of examinations in TEM is still lower at the moment (ca. 10%), because we mainly analyze primers in this device.