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Conservation: Training, Reports (1966-1973): Article 05

Sheldon Keck

Robert L. Feller

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REMARKS Attached are all the conservation statements you so kindly loaned me. Many thanks, indeed — they've been most helpful.

FROM Margaret Gaynor

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SHELDON KECK and ROBERT L. FELLER

Detection of an Epoxy-Resin Coating on a Seventeenth-Century Painting

Received 1/7/63

RECENTLY, a small still-life painting, attributed to an important seventeenth-century master [1], was referred to one of us (S. K.) for conservation. Upon arrival of the piece in this country, it was found that parts of the protective varnish had adhered to the plastic wrapping material, and had been pulled away from the painting when the crate was opened for inspection at U.S. Customs. At the time, there seemed to be little question as to what conservation measures were required. Laboratory examination, however, immediately disclosed complications indicating that treatment would have to await a more thorough examination. The co-author was invited to collaborate, especially in regard to the identification of one particular layer of protective coating. The result of the more detailed examination of the painting resolved a most interesting and noteworthy problem.

STATEMENT OF THE PROBLEM

The painting was said to have been freshly varnished before shipment. Indeed, when it arrived in the laboratory, a pronounced odor of copaiva balsam could be detected, and the surface was found to be still slightly tacky. Tests quickly revealed that the surface coating was extremely thin and was readily removable with xylene. Immediately beneath this readily-removable coating, and covering the surface of the paint, was a comparatively thick, tough, clear film that resisted solvent action. It was this second film that, in a few places, had been torn loose from the paint surface at Customs. The puzzling properties of this tough film, and some of the paint immediately below it, led us to investigate both the coating and the painting in some detail.

EXAMINATION OF THE PAINTING

Examination of the painting under ultraviolet radiation gave no significant information. The painting fluoresced more or less uniformly, slightly more where the surface coating was intact than where it had been torn away. A few minor restorations were faintly indicated by less visible fluorescence.

X-radiographs and infrared photographs revealed the same design as that seen on the surface. The cracks seen in the radiographs gave every indication of being normal age-cracks and appeared to have the same general pattern as those that were observed in the surface of the paint. The evidence of the radiographs and the infrared photographs aroused no suspicion of extensive restoration or over-painting.

Examination of the surface under a stereoscopic microscope at 7 to 30 × magnification revealed numerous areas, particularly in the objects portrayed, where cracks appeared to have been incised in the paint and subsequently filled with a brownish-black material (Figs. 1A and B). Near these cracks, sometimes almost contiguous with them, there seemed to be other cracks partially obscured by translucent paint. These two observations gave the first indication that the painting surface might have been extensively reconstructed.

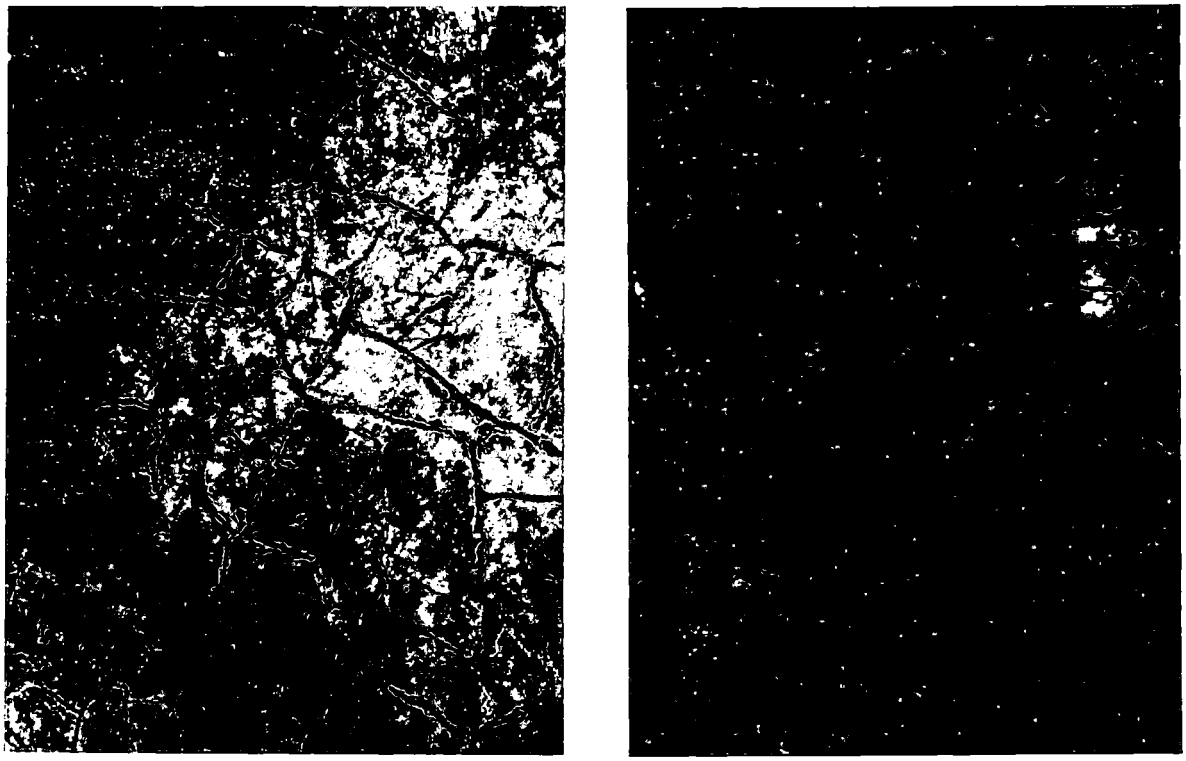

FIG. 1A. *At left* photomacrograph 8×. Surface of painting shows reinforced cracks over what appears to be repaint. Radiograph *at right* of same area enlarged 8× reveals corresponding crackle pattern at lower left but a different one elsewhere.

REMOVAL OF THE TOUGH INSOLUBLE COATING

Preliminary tests had revealed that the thin surface coating was easily removed by xylene, but that the clear tough coating beneath was not. In the torn areas, it was the latter coating that had parted from the paint.

Solubility tests were made to discover how this second coating might safely be removed. None of the usual organic solvents for natural or synthetic thermoplastic resins had any action on the coating at all. It was discovered, however, that when a solvent as mild as xylene was flowed over a test area where the coating had been torn loose, the solvent penetrated between the coating and paint, softening the latter. It was then possible to grasp the free edge of the unaffected coating with forceps and to strip off samples in small sheets. The pale yellow sheets of the film were tough and flexible. They were not brittle and easily broken as would be expected of a natural resin. Removal by peeling in this way could be done only where the xylene had penetrated and weakened the adhesion between the coating and the paint.

In the test area, where the tough coating had been removed, repeated flushing with xylene eventually began to gel the paint. The gelled paint could then be removed by wiping with a cotton swab. The reactivity of the paint to this relatively " mild " solvent suggested the presence of a considerable percentage of natural resin. Examination under the microscope also revealed that the pigment was finely ground, as might be expected in a modern paint.

Removal of the paint that was gelled with xylene uncovered another layer of paint which had remnants of darkened varnish and dirt

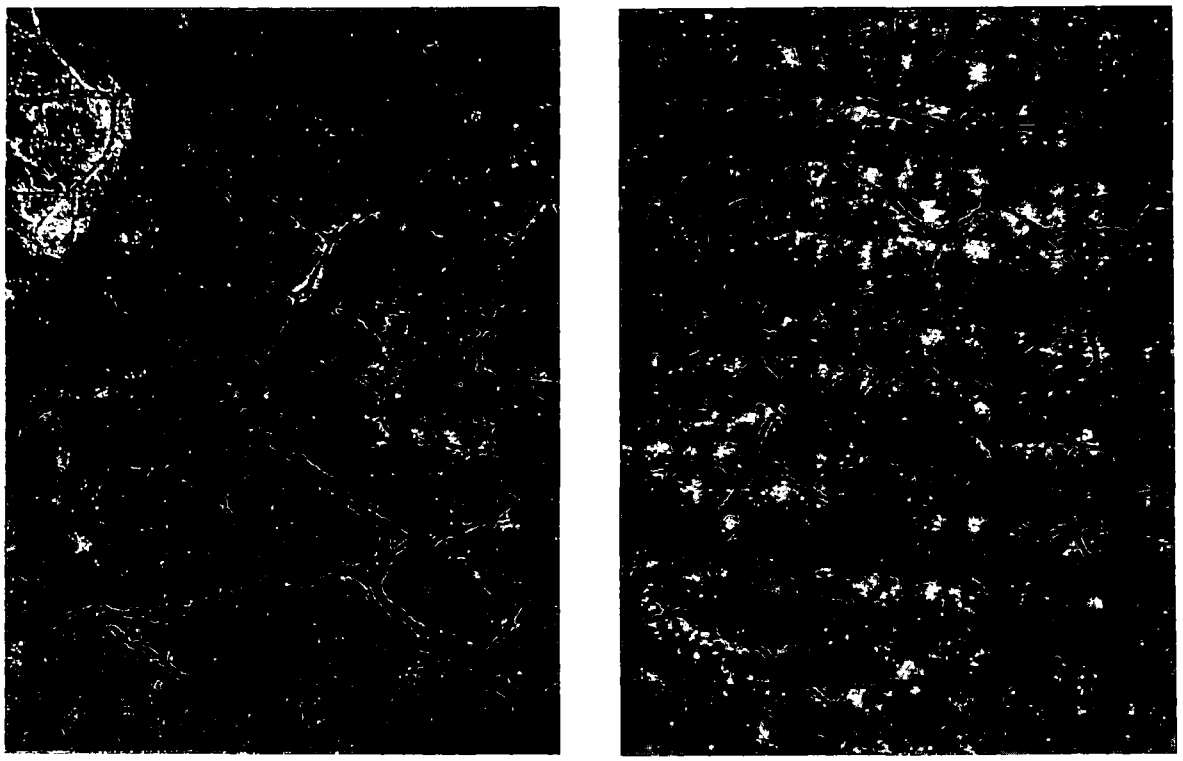

FIG. 1B. *At left* photomacrograph 8×. Cracks in surface of paint, while corresponding in general to those in radiograph *at right*, are clogged by thin overpainting which almost completely obscures finer cracks in the system revealed by X-rays. Test area upper left where insoluble film and semi-opaque overpaint have been removed reveals change in hue and value.

lodged in the interstices of its brushmarks. This lower layer resisted the action of xylene solvent, contained coarsely ground pigments like those often found in paint of the seventeenth century, and possessed a crackle pattern that might be expected in genuinely aged paint (Fig. 1B). Similar tests in a number of other areas revealed the same kind of structure under the insoluble 'second' protective coating, namely (1) a xylene-sensitive paint containing finely ground pigments and possessing a pattern of incised cracks, and (2) a solvent-resistant paint film below it having coarsely ground pigments and a system of cracks which appeared to be genuinely those of age. In each area tested the upper layer of paint was richer in color than the layer it covered, and appeared also to have a more complete range of chiaroscuro.

In the light of the accumulated evidence, a re-examination was made of the entire surface. Careful inspection under a stereoscopic microscope confirmed the earlier indications and led to the following conclusions: (1) almost every detail of the still-life, with the exception of the background, had been reglazed or repainted, apparently to enhance the coloring and modelling. The painting beneath, although to all intents and purposes the same subject, appeared to be without rich coloring, without such full chiaroscuro. (2) Cracks corresponding closely to those in the original paint had been cleverly incised wherever the overpaint was opaque. (3) The design and cracks in the overpaint were so closely identical with those in the original paint that a radiograph had failed at first to indicate that one painting, almost completely new, was superimposed on another. It

was not until the cracks on the surface were compared under low magnification with those in the radiograph that certain areas were found where the incised cracks did not precisely follow those in the painting beneath (Figs. 2A and B). (4) The original subject was probably extensively abraded, if one may judge from what was left of the unrepainted background. (5) A tough, insoluble protective coating had been placed over the repainting, apparently to prevent the readily-softened repaint from detection. On top of this coating had been placed a thin film of readily-soluble material.

ANALYSIS OF THE INSOLUBLE PROTECTIVE COATING

With these conclusions established, there still remained the question of the identity of the tough solvent-resistant coating that had been placed over the work. Samples of the removed film were tested in a wide variety of organic solvents including toluene, benzene, methyl alcohol, acetone, diacetone alcohol, morpholine and dimethyl formamide. The film was not dissolved, gelled, or swelled by any of these. Tests for solubility in water at various temperatures and in dilute solutions of ammonium and sodium hydroxide were equally ineffective.

A sample was prepared and analyzed by infrared spectroscopy. The resulting spectrum corresponded almost identically to spectra reported for high molecular-weight, bisphenol-type epoxy resins [2]. A comparison of the spectra of the unknown and an epoxy resin of this type is shown in Fig. 3 [3]. There is no doubt of the identity of the material. Its spectrum corresponds to that of the known in about twenty absorption bands, and the material itself gave a typical spot test for a bisphenol-type epoxy resin [4].

The only significant difference in the infrared spectra was in the appearance of absorption at 5·9 and 6·05 microns in the unknown. The absorption at 5·9 was thought to be due to carbonyl groups, perhaps in oil, dammar [5], mastic [6], or other natural materials that might have adhered to the film. This supposition proved to be well founded. The spectrum of a sample that was extracted overnight in hot chloroform no longer showed the absorption band at 5·9 microns.

The absorption at 6·05 microns remained after the extraction. It is suspected this band was due to an imino or amide group arising from a curing agent in the polymer. The spectrum in this region most closely resembles that of an epoxy cured with a polyamide: Epon Curing Agent V-15 (Shell Chemical Company) [7].

CONCLUSION

As a result of the examination and analysis, it was concluded that, in all probability, a dull and abraded still-life painting of the seventeenth century had been reconstructed through overpainting, incised patterns of cracks, and a simulated film of aged varnish. This may have been done in order to upgrade a minor painting so that it could be attributed to an important name.

The authors wish to call particular attention to the use of a tough, insoluble epoxy resin in this example, apparently employed to protect solvent-sensitive overpainting from detection. Such attempts obviously run more and more risk of detection today as use of modern investigative techniques and instruments becomes increasingly widespread. As shown in this case, although epoxy resins are insoluble in the usual solvents, identification of the insoluble material can be made with considerable precision by infrared spectroscopy.

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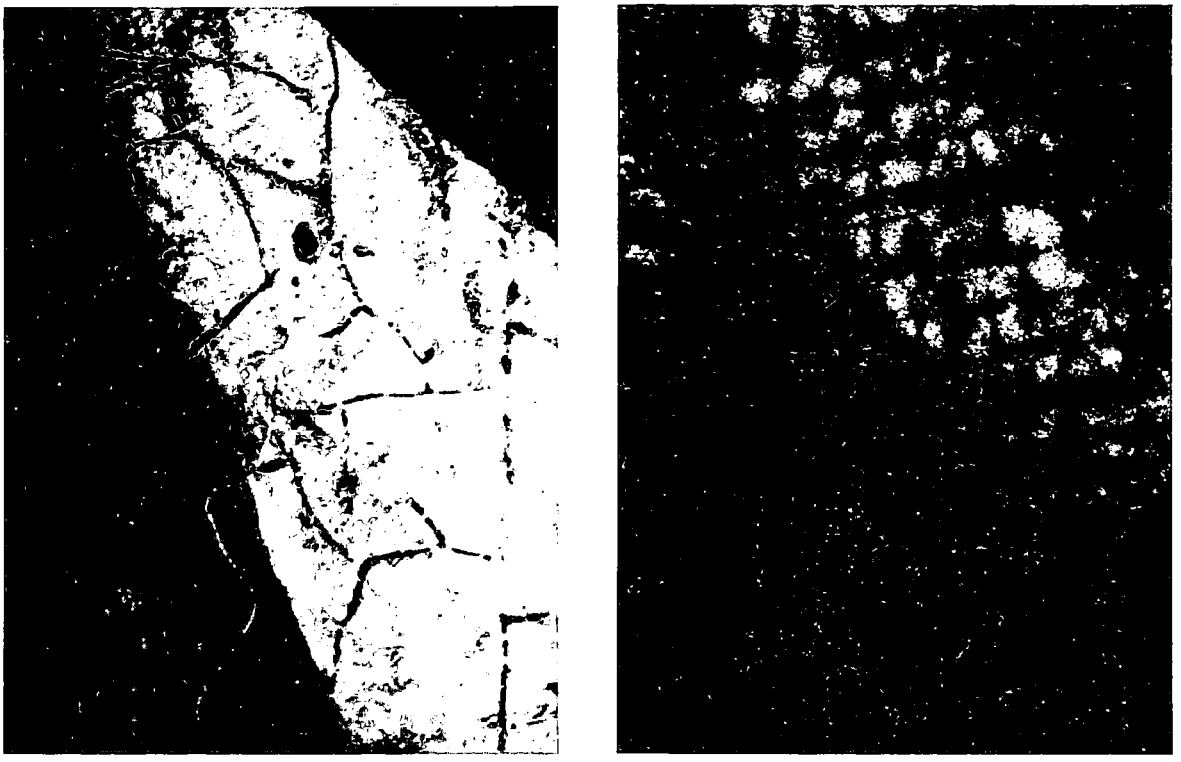

FIG. 2A. *At left* photomacrograph 8×. Repaint with false cracks completely covers paint with a different crackle system as revealed by radiograph 8× *at right.*

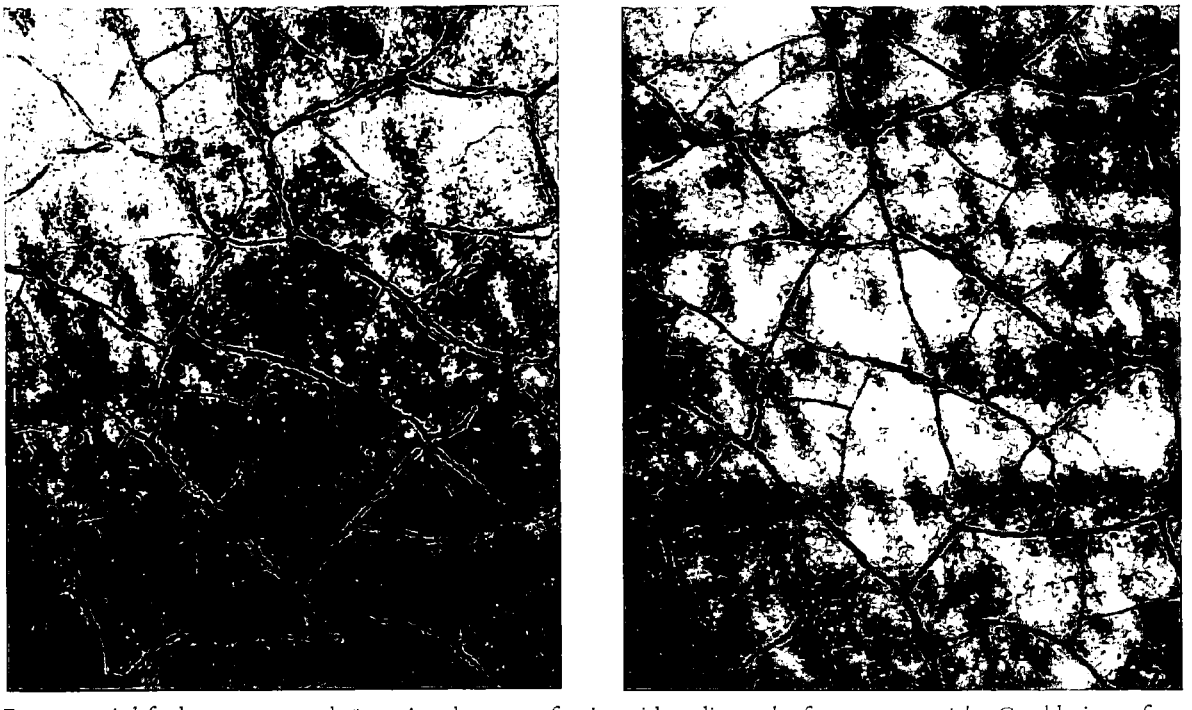

FIG. 2B. *At left* photomacrograph 8×. Another area of paint with radiograph of same area *at right.* Crackle in surface of painting corresponding closely to that in radiograph shows variations and reinforcements which do not quite match the cracks themselves. Note particularly changes in upper left.

Notes and References

1 The painting was in oil on canvas, lined with an aqueous adhesive and a fabric that was aged and brown. Because it is still in private hands, it has not been specifically identified here. The authors returned the painting to its owner, with a complete report of their findings, and made no attempt at conservation.

2 R. E. KAGARISE and L. A. WEINBERGER, 'Infrared Spectra of Plastics and Resins', United States Department of Commerce, Office of Technical Services, *NRL Report 4369*, May 26, 1954.
R. A. NYQUIST, 'Infrared Spectra of Polymers and Resins', Dow Chemical Company, Midland, Michigan, 3rd edition, 1961.
CHICAGO SOCIETY FOR PAINT TECHNOLOGY, 'Infrared Spectroscopy', *Off. Digest*, 33 (1961), no. 434, part 2.
H. L. LEE, 'Infrared Analysis and Epoxy Formulation', *Plastics Technology*, 7 (Feb. 1961), pp. 47–49.

3 The curves in the figure were re-drawn by hand from the instrument charts and may therefore show minor variations in details. The data for the unknown, for example, were re-drawn from a spectrum that was linear with respect to wave number. Analysis was by split mull: the spectrum in the wavelengths below 1300 cm^{-1} was measured in a fluorinated hydrocarbon; that above 1300 cm^{-1} in Nujol. Hence the spectrum in the figure corresponds to the characteristics of the resin, without interference from solvent absorption bands.

4 M. H. SWANN, 'New Spot Test for Epoxy Resins', *Off. Digest*, 30 (1958), pp. 1277–1279.

5 N. W. HANSON, 'Some Recent Developments in the Analysis of Paints and Painting Materials', *Off. Digest*, No. 338 (1953), pp. 163–74.

6 R. L. FELLER, 'Dammar and Mastic Infrared Analysis', *Science*, 120 (1954), pp. 1069–70.

7 The authors are indebted to Mr G. G. Velten, Resins Department, Union Technical Service Laboratory, Shell Chemical Company, Union, New Jersey, for his discussion and suggested identification of the absorption band at 6·05 microns.

DÉPISTAGE D'UN REVÊTEMENT À LA RÉSINE ÉPOXYDE SUR UNE PEINTURE DU XVIIÈME SIÈCLE

Résumé

On examina de manière détaillée une peinture dont quelques parties du vernis avaient été accidentellement arrachées de la surface. Sous une couche mince de vernis très soluble, on trouva une deuzième couche, insoluble dans tous les solvants communs, qui s'était séparée en quelques endroits de la peinture. Le xylène put pénétrer sous cette couche insoluble et amollir et gonfler la peinture. Il fut ainsi possible de retirer au moyen de pinces très fines des couches de ce revêtement. L'examen de ces échantillons par la spectroscopie aux rayons infra-rouges révéla qu'il s'agissait d'une résine époxyde. Cet examen semble démontrer qu'un tableau authentique, quelque peu fendillé, du dix-septième siècle avait été repeint dans une gamme plus riche de couleur et de clair-obscur, pour en améliorer l'aspect et que l'on avait habilement tracé les nouvelles craquelures sur les craquelures originales. Enfin, on avait recouvert le tableau d'une résine époxyde

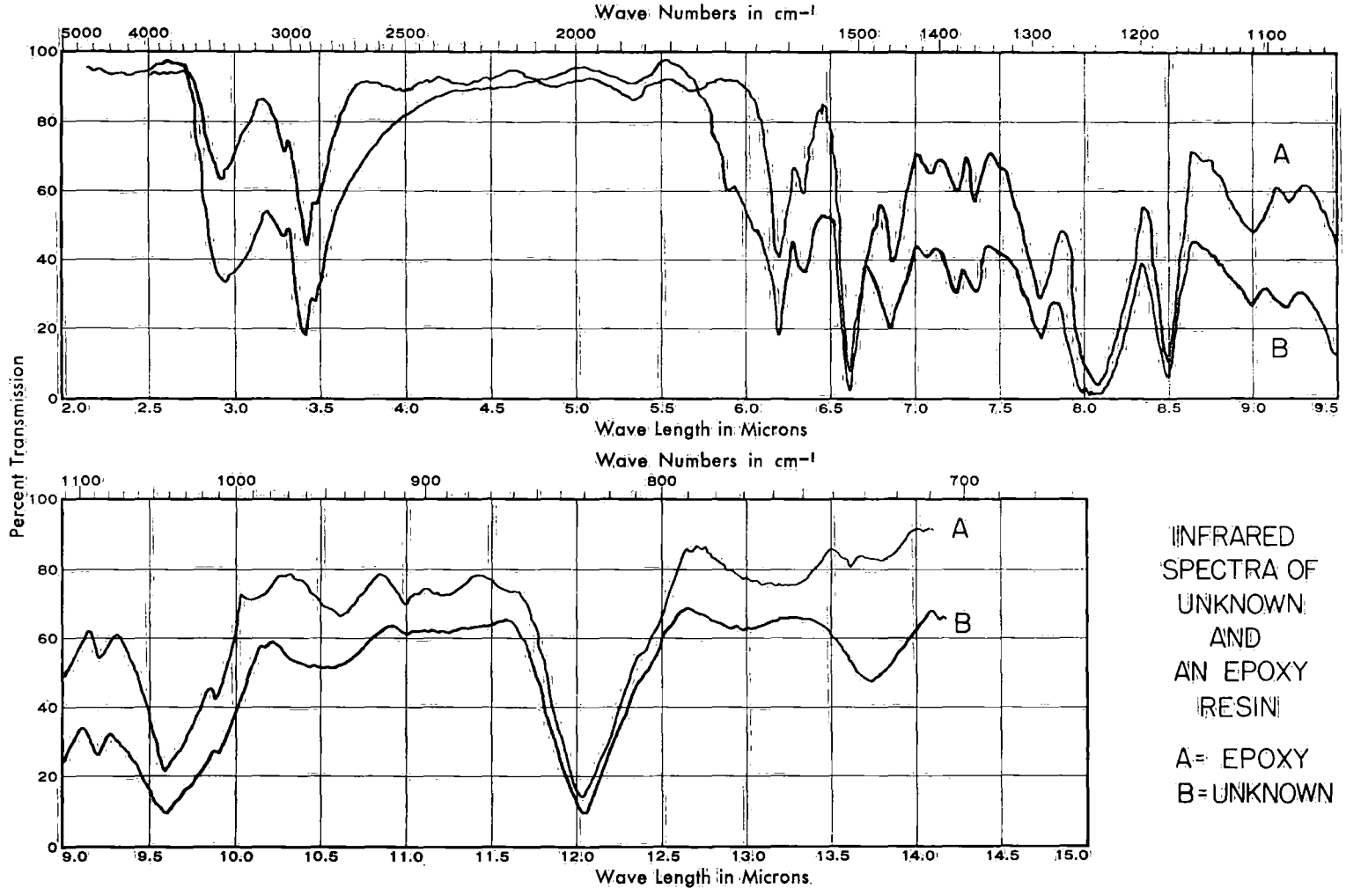
Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
Percent Transmission
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
A
B
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
A
B
INFRARED SPECTRA OF UNKNOWN AND AN EPOXY RESIN
A = EPOXY
B = UNKNOWN

FIG. 3

résistante et insoluble, dans le but d'empêcher le dépistage de la peinture fraîche, plus soluble. En conséquence, les premières épreuves effectuées avec des solvants et l'examen au moyen de photographie aux rayons ultra-violets et infra-rouges ne soulevèrent pas de soupçon, malgré le retouchage étendu du tableau. Nous attirons l'attention des collègues sur cet usage d'une résine époxyde insoluble et sur la précision avec laquelle il est possible de l'identifier par la spectroscopie aux rayons infra-rouges.

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