BLANCHING OF UNVARNISHED MODERN PAINTINGS: A CASE STUDY ON A PAINTING BY SERGE POLIAKOFF

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ABSTRACT
Oil paintings by Serge Poliakoff (1900-69) show a remarkable tendency towards surface blanching. The blanching effect is caused by a whitish blooming, covering parts of the surface. As the paintings of Poliakoff are composed of sharply delimited monochrome geometrical areas, different intensities of blooming could be distinguished related to the type of pigmentation. GC/MS-analyses revealed that the paint layers contain a lot of free fatty acids. This mixture of unsaturated liquid and saturated solid fatty acids migrates to the surface. All unsaturated fatty acids will be degraded by oxidation on the unvarnished surface under the influence of oxygen and light and only the saturated fatty acids remain on the surface as whitish blooming. A treatment with beeswax dissolved in white spirit was applied. No new blooming has been observed two years after this conservation measure.

1 INTRODUCTION

The term blanching, meaning whitish patches appearing on the paint or varnish surface, is used to describe several different phenomena [1]. Numerous causes for blanching as well as some traditional remedies have been proposed. However, in our opinion no satisfying explanations have been given up to now as well as no fool-proof methods for dealing with the phenomena. Therefore blanching is still an open question and an annoyance for both scientists and restorers.

Oil paintings of the French painter Serge Poliakoff [2] show a remarkable tendency towards surface blanching. For no obvious reasons, the blanching of the painting (Fig. 1, see colour plates) described in this article is accompanied by severe damage. In particular, the mechanical properties of this unvarnished painting on linen canvas have changed dramatically.

The goal of these investigations was initially to yield an overall understanding of blanching. However, because of the complexity of blanching phenomena, this study tries in a first attempt to answer the following question: what is the exact nature of the blanched products? which were the pigments and painting media involved with these products? what are the reasons for mechanical alterations of some paint layers? are they related directly to blanching? We hope that the answers will allow the setting up of guidelines for further restoration treatment, particularly for preventing further blanching.

2 ANALYTICAL PROCEDURES

2.1 *Analytical methods*

The methods used for standard pigment analysis, for example optical microscopy, microchemistry, optical emission spectroscopy (OES), X-ray powder diffraction (XRD) and diffuse reflectance spectrophotometry, are described elsewhere [3, 4]. Synthetic pigments were identified by thin-layer chromatography (TLC) [4, 5]. The paint media and blanched products were examined by gas chromatography/mass spectrometry (GC/MS) and the results were presented as total ion chromatograms [6].

2.2 *Sampling and sample treatment*

The samples were taken mechanically. For GC/MS analyses, sampling was followed by sample treatment. The steps of sample preparation as well as the method itself are explained in full elsewhere [3, 6]; however, some steps of sample treatment are described below.

3 THE PAINTER'S TECHNIQUE

3.1 *Description of the painting*

The painting on canvas discussed here, 'Composition Without Title' (Fig. 1, see colour plates), was done in the late 1950s by Serge Poliakoff (born Moscow, 1900; died Paris, 1969), a painter of the Ecole de Paris ('l'art informelle'). With its geometrical structure, its sharp outlines and its contrasts of light and dark, the painting is very characteristic of the artist.

The composition is divided into seven different-coloured geometric areas, which are meshed together. Each area is uniform in its texture and colour. There are two yellow, two light red and two dark red areas and one green area.

3.2 *Pigments and paint media*

As is demonstrated by OES, XRD and TLC analyses, a small palette of pigments has been used. A red lake is the major pigment found in the dark red paint layer, with minor amounts in the light red. It has been identified as alizarin precipitated on a substrate embodying aluminium and calcium (Pigment Red 83). While the dark red paint layers contain only this alizarin lake, a further synthetic organic pigment, toluidine red (Pigment Red 3) [7, 8] predominates in the light red paint layers.

The yellow paint layers are pigmented with chrome yellow and some Prussian blue. In the green paint layer a mixture of cobalt green, Prussian blue, chrome yellow and titanium white could be identified. The titanium white pigments in the dark red, light red and yellow paint layers are agglomerated into thick clumps (Fig. 2) and were therefore not uniformly dispersed in the paint medium. The examination showed that titanium white was blended with zinc white, which is unusual for oil vehicles.

Fig. 2 Detail of the yellow areas showing thickened clumps of titanium white and parts of the red paint layer underneath shining through, ×5.

Paint medium analysis has been conducted on samples taken from all areas and paint layers by extracting the medium and subjecting it to GC analysis, the procedure for which is described elsewhere [9]. These analyses resulted in the characteristic fatty acid profile of linseed oil. There was no indication of the presence of a proteinaceous medium.

3.3 *The layer structure of the painting*

The canvas is covered with a dark red paint layer containing linseed oil, alizarin lake and some toluidine red. All other areas were painted on top of this dark red layer. The green colour was applied very thickly, whereas the yellow was superimposed as a very thin layer (Fig. 2). The painting remained unvarnished.

From: Cleaning, Retouching and Coatings, Technology and Practice for Easel Paintings and Polychrome Sculpture, IIC Preprints 1990, Eds. J.S. Mills and P. Smith, p. 138 - 143.

4 OPTICAL EXAMINATION OF THE BLANCHED AREAS

Almost the entire area except the green field was affected by blanching. However, the degree of blanching could be related to the colour of the areas. The most affected parts were the two light red areas (Figs. 1 and 3). As mentioned, blanching there was accompanied by mechanical alterations: these paint layers show a leached and embrittled appearance. Surface blemishes like crow's-foot cracks, cleavage, flakes and losses could be observed.

Fig. 3 Detail of the light-red areas showing the roughness of the surface and some of the mechanical damage.

Another troublesome defect should be noted: masses of fine particles (besides the thick white clumps mentioned before) are dotted all over the light red areas (Fig. 3), looking like incompletely dispersed pigments projecting through the surface and giving the impression of emery paper. However, the green area was affected neither by blanching nor by defects of the surface structure (Fig. 4), except the margin with the dark red area where the green paint layer is thinly superimposed upon the dark red (Fig. 5).

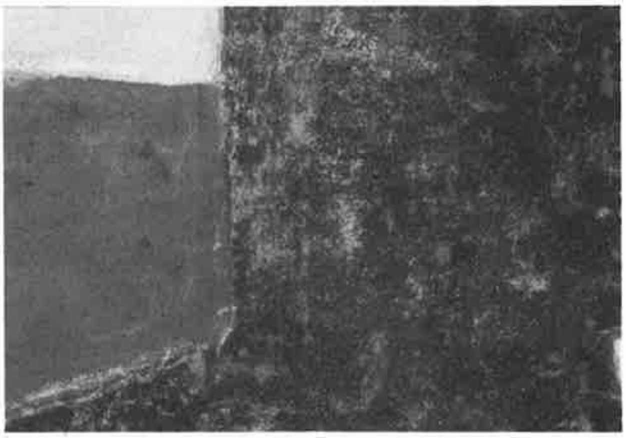

Fig. 4 Detail of the green and dark red areas.

Blanching on all affected areas was also examined by optical microscopy and that led to the conclusion that blanching is essentially a surface phenomenon. Under the microscope blanching appeared as an agglomeration of tiny needles covering the coloured surfaces like a bloom. These 'crystals' could be easily removed by a scalpel and their hardness was very low. The needles showed a whitish or transparent appearance, scattering the light in all directions. Diffuse reflectance spectrophotometry revealed the whitening effect of these 'bloom needles' and XRD characterized the material as being highly amorphous.

Fig. 5 Detail of the green and dark red areas, ×10.

5 PAINT MEDIA ANALYSES

5.1 *GC/MS analyses of the blooming*

A series of bloom samples was taken from all areas. These soft and low-melting needles turned out to be completely soluble in hexane. GC/MS analyses of the hexane solutions revealed a similar composition for all bloom samples investigated: they contained a mixture of palmitic and stearic acid accompanied by only a small and varying proportion of azelaic acid. Palmitic and stearic acid are solid fatty acids [10]. The peak ratios in the total ion chromatogram of Figure 6 illustrate the fatty acid profile for a bloom sample taken from the dark red area. With only two exceptions, palmitic and stearic acid appeared in a ratio of about two to one and were therefore close to their eutectic composition of 70:30 [10, 11]. Since a eutectic mixture of two (or more) substances will have the lowest possible melting point, in this case considerably lower melting points (8-15°C) emerged for the fatty acid mixture than for the pure palmitic or, particularly, stearic acid [11]. This explains the softness of the bloom crystals.

5.2 *GC/MS analyses of the paint medium*

Although blooming of this type appeared to be associated with changes in the medium, there was no explanation available for the mechanism by which these fatty acids could migrate to the surface. To reveal the migration mechanism and to demonstrate possible changes in the medium a series of paint samples was taken.

As described elsewhere, different classes of compounds, for example free fatty acids, triglycerides and metal soaps, can be extracted step by step from any aged linseed oil medium [6]. In our case, the total amount of medium which could be extracted from blanched paint layers was very high, even in samples taken from the leached-looking light red areas. In every sample of blanched paint examined, a proportion of paint medium considerably greater than 50% of that of the pigment must be assumed. Within this total extract the proportion of triglycerides was the largest, followed by a moderate proportion of free fatty acids and a small proportion of metal soaps, probably containing zinc soaps deriving from the blended titanium white.

5.2.1 *Free fatty acids*

Extraction and solution testing again revealed all free fatty acids as being soluble in hexane. The total ion chromatogram of the hexane extract of a sample taken from the dark red field is shown in Figure 7. In addition to the (solid) saturated fatty acids identified in the bloom samples (Fig. 6) we found a (liquid) unsaturated fatty acid, oleic acid. As to the amounts of the different fatty acids in Figure 7, it must be stressed that the analyzing system used here is more sensitive for saturated than for unsaturated fatty acids. Therefore, in the case of the sample taken

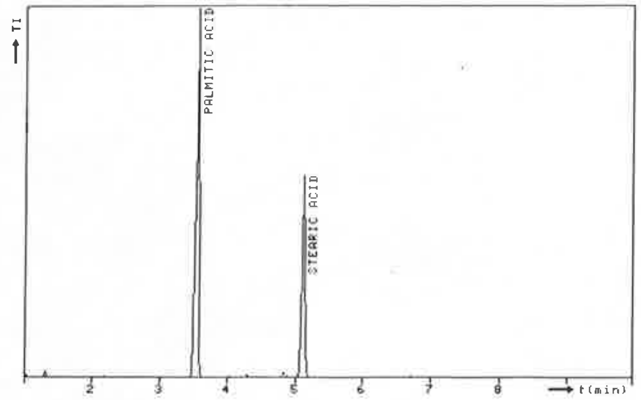

Fig. 6 'Blooming': fatty acids, dark red area; hexane solution.

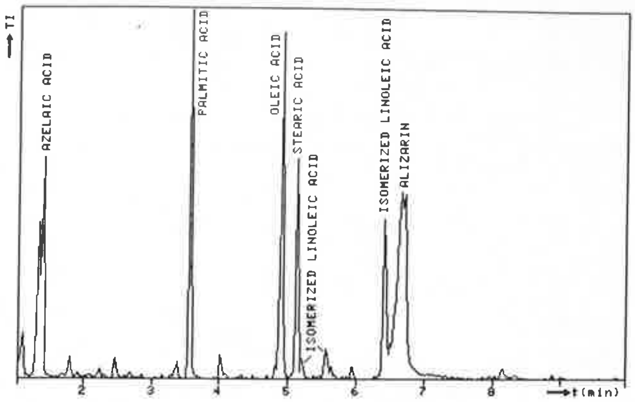

Fig. 8 'Triglycerides': fatty acids, dark red paint layer; chloroform extract.

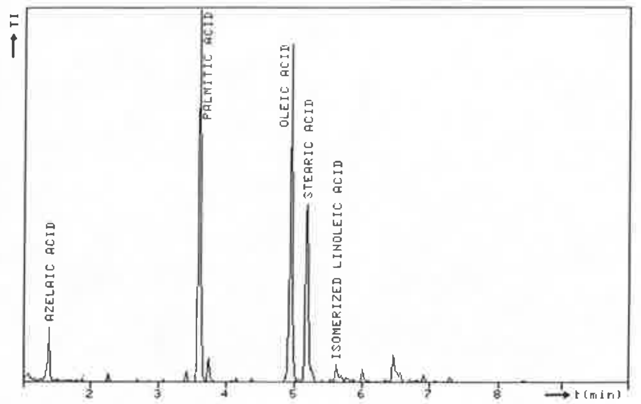

Fig. 7 'Free fatty acids', dark red paint layer; hexane extract.

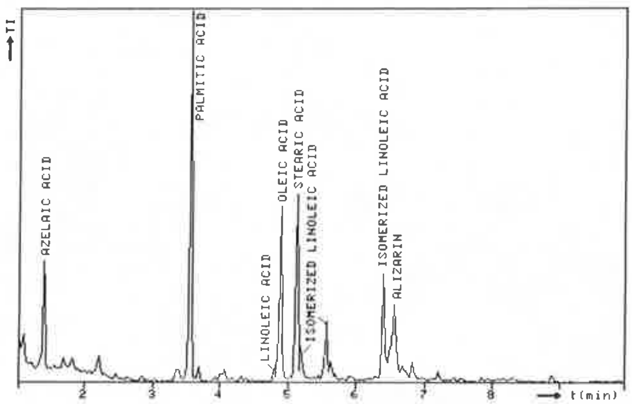

Fig. 9 'Metal soaps': fatty acids, dark red paint layer.

from the dark red area, the amount of oleic acid is even greater than the combined amounts of palmitic and stearic acid. The results for free fatty acids were only slightly different for all other samples.

The detection of the low melting oleic acid (m.p. = 13.3°C (α) or 16.3°C (β) [10]) may yield an explanation for the migration mechanism: since oleic acid is a liquid at ambient temperatures, its mixture with stearic and palmitic acids (in the given relations of the free fatty acids in the paint medium) also produces a liquid and therefore a product able to migrate.

5.2.2 *Triglycerides and metal soaps*

The triglycerides and the metal soaps were analyzed with the help of the fatty acids released from these compound classes. Analyses of triglycerides were carried out on samples previously leached with hexane to remove all free fatty acids. The triglycerides were then extracted with chloroform from these residues, the extracts saponified and the fatty acids methylated and analyzed by GC/MS. With acidified methanol an additional fraction of fatty acids was liberated from the metal soaps in the remaining samples, again methylated and subjected to GC/MS analysis. The resulting total ion-chromatograms are shown in Figures 8 ('Triglycerides') and 9 ('Metal soaps') and illustrate the presence of dicarboxylic acids (azelaic acid), saturated fatty acids (palmitic and stearic acids), unsaturated fatty acids (oleic and mainly isomerized linoleic acids) and an accompanying 'impurity', alizarin. With respect to the fatty acid profile of palmitic, oleic and stearic acids, an obvious similarity could be detected between the free fatty acids (Fig. 7) and the triglycerides (Fig. 8).

5.2.3 *Isomerized fatty acids*

As shown in Figures 7 to 9, isomerized unsaturated fatty acids (linoleic acids) occurred in the free fatty acids, the triglycerides and in the metal soaps. These isomerized linoleic acids, formed by cis-trans rearrangements of the double bonds, revealed a heating procedure for these oil media which is usually associated with stand oils [12-14]. This observation and a ratio of palmitic/stearic acid of 2:1 (Figs. 6-9) as well as the great amount of free fatty acids soluble in hexane are typical for linseed stand oil [11].

5.2.4 *The medium in the green area*

In principle, GC analyses from the unblanched green area revealed no qualitative differences compared to the other areas. However, a quantification made it obvious that the amount of oil vehicle in the green layer, though more fatty in its appearance, is remarkably lower than in the other areas, not reaching even one half. At the same time, the proportion of the triglycerides is the highest. Moreover, the amount of fatty acids released from metal soaps was considerable, whereas the proportion of free fatty acids was small. Finally, within these free fatty acids the relative proportion of oleic acid was smaller (Fig. 10) than in samples from blanched areas (Fig. 7).

This small amount of free fatty acids and a total lack of isomerized linoleic acids indicate the use of cold-pressed linseed oil rather than stand oil in the green paint layer [6].

6 CAUSES OF BLANCHING

6.1 *The mechanism of blooming*

Saturated fatty acids like palmitic and stearic acid undergo no important changes during the aging processes (e.g. drying) of oil media. Therefore the characteristic fatty acid profiles of these two acids remain substantially unchanged and can be used for oil identification [9]. For the same reasons, identical fatty acid profiles in the bloom, as well as in the free fatty acids, the triglycerides and the metal soaps of the paint layer below, proved

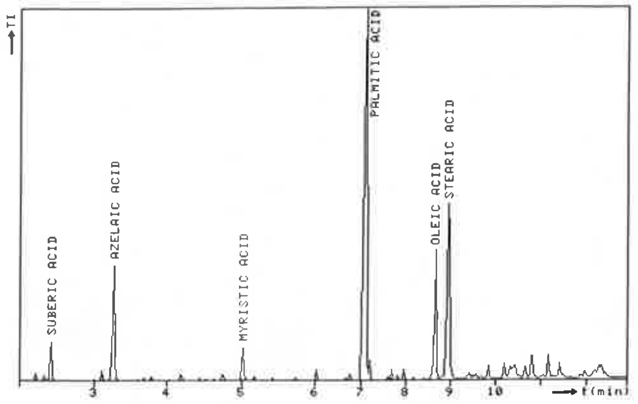

Fig. 10 'Free fatty acids': green paint layer.

beyond all doubt that the fatty acids in the bloom originate from this paint layer.

All linseed stand oils, as used in the blanched paint layers, contain a high proportion of free fatty acids deriving from their process of production [11]. In this process heating is conducted under exclusion of air and, unlike the boiled oils, unsaturated fatty acids are therefore not oxidized but only isomerized, as in the case of linoleic acid [12-14]. This results in a liquid mixture of fatty acids as shown in Figure 6. If not mixed with basic pigments (e.g. lead white) which 'consume' free fatty acids by soap formation and initiate an additional film formation process [15], these fatty acids remain mobile in the paint layer. Since on our painting the blanched paint layers are mixed only with the inactive titanium dioxide, these fatty acids are able to migrate. By migration at least some parts of the mixture appear at the unvarnished surface. The liquid unsaturated fatty acids exposed to the influence of light and oxygen are now subject to disruptive oxidations. Some possible oxidation products, like nonanoic acid or nonanal in the case of oleic acid, evaporate in the course of time; among the others azelaic acid, for example, is deposited in a fixed form at the surface. Then the remaining solid saturated fatty acids crystallize as a loose bloom.

For reasons described above, linseed stand oils are known to be a possible cause of blooming [16, 17]. Though blanching has occurred in other cases in combination with linseed oil [18, 19] it is nevertheless inadmissable to associate blanching primarily with linseed oil media. In particular, the free fatty acids in the oil vehicle should not be seen as a major disadvantage. Because of their great wetting power, higher amounts of free fatty acids in oils are very useful for grinding some pigments, and in old paint layer films they are useful for their plasticizing effects [20]. Under no circumstances should these free fatty acids be removed by leaching.

The migration and oxidation processes described above to illustrate the mechanism of blooming do not really reveal the causes of this phenomenon. In particular, there is no obvious explanation as to why fatty acids migrate to the surface only in some special cases. Therefore causes originally not associated with the oil medium must be considered, in particular the pigmentation and problems deriving from it, as for example pigment-vehicle interactions and film porosities.

6.2 *Unsuitable pigmentation*

In such a simple layer structure as in our painting, where the paint is applied directly (without the classic ground) to the support and has no varnish over it, even small accidents are apt to cause damage. This bad structure is emphasized by an unsatisfactory pigmentation in the blanched areas. Toluidine red, titanium dioxide and alizarin lake are not very suitable for oil media [8, 15, 21-23].

6.2.1 *The role of the alizarin lake*

Where the painting is affected by blanching, alizarin lake either exists in the paint layers on top or in paint layers underneath. As in the case of the yellow fields, these layers are covered by a thin layer so that the red layer below shines through (Fig. 2). As mentioned, blanching does not occur in those parts of the green field where the red paint layer is covered by a thick non-transparent green film. Therefore blanching seems to be somehow associated with the occurrence of alizarin lake.

According to Eibner [23], alizarin lake generates some problems in oil vehicles. It consumes great amounts of oil (60-70% of the pigment content) and it delays the drying process. If not mixed with lead white, drying cracks, for example of the crow's-foot type, appear [20].

As alizarin lake is of no further technical importance, no specific investigations were available concerning its behaviour in aged oil films. Therefore the assumed special influence of alizarin lake on blooming could not be further elucidated.

6.2.2 *The role of the titanium white pigment*

Unfortunately, these red paint layers were not mixed with lead white, which supports film formation and has a stabilizing effect, especially on unsatisfactory oil paint formulations. A blended titanium white (TiO_2) was used instead. All our attempts to identify this pigment more exactly by XRD as being anatase or rutile were unsuccessful. In our experience this happens quite often. Titanium white in respect to film formation is at best quite inert (rutile-type TiO_2) or even has a retarding effect (anatase-type TiO_2) [15]. However, commercial TiO_2 pigments are normally modified by surface coating. In the case of our painting the titanium white samples analyzed by OES contained, besides Ti, considerable amounts of Zn, Si and Al. We therefore assumed a very common commercial TiO_2 pigment, blended with zinc white and surface treated with Al_2O_3 and SiO_2 [22, 24].

Probably the most important property of these pigments influencing the pigment-vehicle behaviour is the charge residing on these coated surfaces. In stand oil vehicles large amounts of smaller molecular weight species are attached from the paint medium. Metal soaps and free fatty acids are especially strongly adsorbed [22, 24, 25]. TiO_2 pigment particles with adsorbed layers of paint medium components tend to form loose clusters (flocculation), thereby reducing the degree of dispersion. Flocculation starts immediately after the titanium white pigments are dispersed in the paint formulation and is helped by the retarded start of the drying process in these paint layers.

The zinc white content of the titanium white pigments additionally causes a damaging agglomeration process which is very characteristic for paint formulations of stand oils with basic pigments [11]. During drying and aging of the paint film, zinc soaps are formed, especially with stearic and palmitic acids which agglomerate to form large and firm particles using the titanium white flocculates as nucleus of agglomeration [24, 26]. As the volumes and the weights of the surrounding paint medium can be considerably reduced by losses during the drying and aging processes, these large particles can now project through the film surface as can be seen in Figures 2 and 3. To avoid these thickened clumps, the compatibility of stand oil formulations with zinc white must be proved before mixing [11].

All these reactions would produce inhomogeneities in the paint layer and a strong unevenness or roughness of the surface, accompanied by loss of gloss. Besides this gloss haze, strongly emphasizing the blanching phenomenon, another effect with particular relevance to possible blooming mechanisms must be considered. Zinc soaps of palmitic and stearic acids would be concentrated above the paint surface and exposed to the air. Moisture would be adsorbed, particularly on pigment particles containing zinc

[24]. Palmitic and stearic acids desorbed in this way or released from zinc soaps by hydrolysis then appear immediately on the surface. This mechanism corresponds with the observed increase of the blooming with rising humidity.

6.2.3 *The toluidine red haze*

Toluidine red provides a bright red of acceptable lightfastness when used in full shade. In tints with whites such as titanium dioxide (as observed here) lightfastness is very poor. The pigment bleeds in organic solvents and also shows poor drying properties in oils [7, 8]. For these reasons, surface blemishes are well known in technical paint formulations pigmented with toluidine red and containing an air-drying vehicle [8, 21]. In these cases, innumerable agglomerated pigment particles covered with a film of paint medium project from the surface, producing a dull and rough impression. This effect is similar to those described in the previous section, except for the smaller size of the agglomerates. The extensive surface damage in the light red paint layers is probably caused by the cumulative effect of these two similar actions by unsuitable pigments. It is therefore not surprising that all other paintings of Poliakoff investigated, pigmented in the red paint layers with toluidine red, showed surface blanching and blooming.

6.3 *Porosity*

As concerns their materials, pigments as well as vehicles, the dark red, light red and even the yellow paint layers of this painting are typical not of artists' colours but of technical paint formulations. However, these paint layers differed from technical paint films in two points. Firstly, there were no stabilizing compounds (e.g. surface active agents) added and secondly, the proportion of pigments was considerably greater than in technical paints. Both circumstances produced unfavourable consequences. The lack of additives was responsible for flocculation and agglomeration described above. Together with the agglomeration processes the higher amounts of pigments in the paint layers resulted in porous films. While the adsorbed vehicle layers in the agglomerated particles are still present [27], the available volume between the pigments in the surrounding aged film could no longer be filled with the paint medium remaining. The resulting porous structure facilitated migration processes and reduced mechanical stability.

7 MEASURES AGAINST BLANCHING

Blanching phenomena described in the literature have occurred both on works of art [1, 18, 19, 28] and on technical paints [8, 16, 17, 21].

The questions to be put were, firstly, 'Could the measures described in these articles, or parts of them, be adopted?' and, secondly, 'Did the examination of the painting by Poliakoff presented here give a system of 'dos' and 'don'ts' demanding special measures?'.

7.1 *Traditional measures*

Wyld *et al.* [19] specify a number of traditional methods of treatment, such as rubbing with egg or oil, treatment with solvents, scraping off the top layer of the paint, 'Pettenkof(f)ering', and the use of heat. Whereas the use of dimethylformamide vapour is also accepted in the reforming of blanched oil paintings [18], these methods were not recognized as scientific but related to 'folklore'. However, in special cases, slower evaporating solvents such as diacetone alcohol, glycol, cellosolve solvent, cellosolve acetate, morpholine, triethanolamine, dimethylethanolamine [28] and dimethylformamide could be used successfully for reforming blanched oil paintings.

Probably most of these solvents would at least be able to remove bloom crystals by dissolving them. Unfortunately these methods could not be applied to our painting because of the solubility of the toluidine red pigment in these solvents, causing bleeding, and because of possible subsequent solvent action, especially by those solvents containing amino groups with the weakened vehicle (aminolysis [29]), which could not be predicted. For similar reasons, all measures had to be avoided which provided only temporary effects and probably initiated disadvantageous actions subsequently. Above all, volatile solvents and 'Pettenkof(f)ering' had to be vigorously rejected. Likewise the use of heat would remove bloom only temporarily and new migration processes of lower melting mixtures (eutectics) might be set in action.

7.2 *Applied measures*

Surfaces of technical paints showing blanching phenomena comparable to our case, composed of bloom and gloss haze, were always treated in the same way: the bloom particles are removed mechanically and the surface is then covered with a thin clear coating. These measures achieve the removal of the bloom particles without solvent effects; the prevention of migration processes by filling the pores; and the protection of the surface against light, oxygen and moisture. Even gloss hazes might be reduced by coating and therefore smoothing the surface.

However, in our case the artist beyond doubt intended a surface which was not glossy, not varnished, and slightly rough in texture. Therefore, since varnishing was not possible, surface blemishes caused by the pigment particles projecting through the surface must remain unchanged. During the treatment finally carried out, the bloom was removed with a dry swab and the surface was subsequently impregnated with a 5% solution of beeswax in white spirit.

The goal of this method was firstly to fill the pores on the paint layers with wax to prevent further migration processes. Secondly, the surface and particularly the projecting particles would be covered thinly with wax to prevent or at least to reduce the adsorption of water which would otherwise cause the desorption of fatty acids, which would then appear again as bloom on the surface.

It should be emphasized that this treatment met the crucial aesthetic demands mentioned above, in particular not changing the optical characteristics of the painting. Thus at least the most disturbing surface phenomenon was eliminated and no bloom has been observed two years after the application of this wax impregnation method.

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REFERENCES

1 Collection of statements on 'Blanching' with contributions by D. Bull and R. Shepherd, J. Hargrave, B. Jessell, S. Rees Jones, H. Lank, T. Lindsay, H. Ruhemann, IIC-United Kingdom Group, London (1968).

2 Oellers, A.C., 'Poliakoff, Serge' in *Handbuch Museum Ludwig*, Cologne (1979).

3 Burmester, A., and Koller, J., 'Known and new corrosion products on bronzes: their identification and assessment, particularly in relation to organic protective coatings' in *Recent Advances in the Conservation and Analysis of Artifacts*, Summer Schools Press, Institute of Archaeology, University of London (1987) 97-103.

4 Burmester, A., and von Lüttichau, M.-A., 'Gib meine Jugend mir zurück. Korrekturen zum malerischen Werk von Hans Schmithals', *Die Kunst* 10 (1987) 826-834.

5 Strauss, I., 'Übersicht über synthetisch organische Künstlerpigmente und Möglichkeiten ihrer Identifizierung', *Maltechnik/Restauro* 90 (4) (1984) 29-44.

6 Koller, J., 'Technische Beobachtungen zur 'Himmelfahrt Mariae' aus

dem Bamberger Dom, Teil 3: Die Untersuchung der organischen Malmaterialien' in *Die Bamberger 'Himmelfahrt Mariae' von Jacopo Tintoretto,* Arbeitsheft 42 des Bayerischen Landesamtes für Denkmalpflege, Munich (1988) 137-145.

7 Potdar, S., 'Toluidine, para, and chloronitraniline reds' in Lewis, P.A., (ed.), *Pigment Handbook,* Vol. I, 2nd edition, New York (1988) 441-452.

8 Herbst, W., and Hunger, K., *Industrielle organische Pigmente,* Weinheim (1987) 139-147 and 277-287.

9 Mills, J.S., 'The gas chromatographic examination of paint media. Part I. Fatty acid composition and identification of dried oil films', *Studies in Conservation* 11 (1966) 92-107.

10 Brockmann, R., Demmering, G., Kreutzer, U., Lindemann, M., Plachenka, J., and Steinberner, U., 'Fatty acids' in Gerhartz, W., (ed.), *Ullmann's Encyclopedia of Industrial Chemistry,* 5th edition, Weinheim (1987) 245-276.

11 Kaufmann, H.P., *Analyse der Fette und Fettprodukte,* Berlin (1958) Vol. I, 665-670 and Vol. II, 1529-1531.

12 Wexler, H., 'Drying oils' in Mark, H.F., (ed.), *Encyclopedia of Polymer Science and Technology,* Vol. 5, New York (1966) 216-234.

13 Hires, J., Krejzar, E., and Mleziva, J., 'Cis-trans-Isomerisierung ungesättigter Fettsäuren im Laufe der Alkydharz-Herstellung', *Fette, Seifen, Anstrichmittel* 69 (1967) 241-245.

14 Helme, J.P., and Molines, J., 'Spectres infra-rouges de l'huile de lin. Applications aux standolies, résines glycérophtaliques et huiles modifiées', *Peintures, Pigments, Vernis* 33 (1957) 524-543.

15 Bell, S.H., 'The structure of paint films', *Journal of Oil and Colour Chemists' Association* 38 (1955) 595-623.

16 Hörner, A., 'Blauanlaufen von pigmentierten Außenanstrichen. Wirkung, Ursache und Abhilfe', *Deutsche Farben-Zeitschrift* 8 (1954) 279-282.

17 Kaufmann, H.P., 'Über Glanzschäden bei Anstrichfilmen I: Das Blauanlaufen', *Fette und Seifen* 55 (1953) 681-685.

18 Lank, H., and Pemberton-Pigott, V., 'The use of dimethylformamide vapour in reforming blanched oil paintings' in Brommelle, N.S., and Smith, P., (eds.), *Conservation and Restoration of Pictorial Art,* London (1976) 103-109.

19 Wyld, M., Mills, J., and Plesters, J., 'Some observations on blanching with special reference to the painting of Claude', *National Gallery Technical Bulletin* 4 (1980) 49-63.

20 Talen, H.W., 'The requirements for the prediction of paint performance', *Journal of Oil and Colour Chemists' Association* 46 (1963) 940-974.

21 Herbst, W., and Merkle, K., 'Untersuchungen gestörter Oberflächen pigmentierter Systeme', *Farbe und Lack* 75 (1969) 1137-1157.

22 Ritter, H.S., 'Surface properties of titanium dioxide pigments' in Patton, T.C., (ed.), *Pigment Handbook,* New York (1973) Vol. III, 169-184.

23 Eibner, A., *Malmaterialienkunde als Grundlage der Maltechnik,* Berlin (1909) 204-205.

24 Doorgeest, T., 'Adsorption and desorption phenomena on pigment surfaces' in *FATIPEC Congress 1962,* Weinheim (1962) 93-97.

Doorgeest, T., 'Adsorption of water vapour, stearic acid, stearyl alcohol and stearic acid modified alkyd resins on the rutile titanium-dioxide pigments', *Deutsche Farben-Zeitschrift* 22 (1968) 33-34.

25 Rothstein, E.C., 'Nature of pigment surfaces' in Patton, T.C., (ed.), *Pigment Handbook,* New York (1973) Vol. III, 131-138.

26 Bult, R., 'Körnchenbildung und Glanzverlust bei Titandioxid/Zinkweiß-Alkydharzanstrichen', *Farbe und Lack* 72 (1966) 842-850.

27 Stieg, F.B., 'Pigment/binder geometry' in Patton, T.C., (ed.), *Pigment Handbook,* New York (1973) Vol. III, 203-217.

28 Bergeon, S., Mondorf, G., Delbourgo, S., and Rioux, J.-P., 'Le blanchiment: un cas precis d'étude' in *ICOM Committee for Conservation, 6th Triennial Meeting,* Ottawa (1981) 81/20/3, 1-8.

29 Kappelmeier, C.P.A., 'Aminolyse als Hilfsmittel bei der chemischen Analyse von Kunstharzen', *Fette, Seifen, Anstrichmittel* 57 (1955) 229-230.

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John Larson: The treatment and examination of painted surfaces on eighteenth-century terracotta sculptures, pp 28-32

Fig. 8 (above) Cross-section of paint layers on a terracotta by Scheemakers. In all there are about 12 layers.

Fig. 9 (right) Portrait of Monsieur Ducis by Pajou, showing the bust half-cleaned.

Johann Koller and Andreas Burmester: Blanching of unvarnished modern paintings, pp 138-143

Fig. 1 Serge Poliakoff: 'Composition Without Title', private collection, late 1950s, oil on canvas, 65cm × 81cm, before restoration treatment.