



ARCHLAB ACCESS REPORT

Call number: **15th February call/March 2017-September 2017**

Title of the ARCHLAB TNA Project: **KETONE RESIN VARNISHES on Munch Museum's Paintings:**

An interdisciplinary, transnational research

Project Acronym: **KV-MUM-P**

User Group:

Name and forename(s) User Group Leader: **Irina Crina Anca Sandu**

Institution: **Munch Museet – Conservation Department**

Name of other researchers of the User Group: **Eva Storevik-Tveit, Charlotte Stahmann**

ARCHLAB Providers/home institution: **Opificio delle Pietre Dure in Florence/RCE in Amsterdam/
CATS-SMK in Copenhagen**

Contact person ARCHLAB Provider/home institution: **Monica Galleotti & Giancarlo Lanterna /Ineke
Joosten/ Pauline Lehmann Banke and Sanne Bouwmeester (Staatens Museum for Kunst)**

Period of the visit: **8-10th of May 2017/7-8th of June/20-22nd of September**

Date of the report: **6.11.2017**

Background to the project:

The research project running at the Conservation Department of the Munch Museum (MUM) in Oslo from December 2016 until end of 2018 aims to:

- map the extent of Munch paintings in the collection affected by AW2 varnish applied in earlier treatments,
- study the chemical and physical nature of AW2 resin and other ketone resins that were applied on the paintings (late 1950's to the beginning of the 1980's),
- understand the origin of the observed degradation-deterioration patterns and their effect on the underneath paint layer.

This knowledge will provide the base for establishing a **suitable methodology** for the **removal** of the degraded varnish if necessary.

From the **internal survey** performed on conservation reports the following data emerged:

- **16 paintings** are varnished with **AW2** - between 1957 – 1970,
- 14 paintings are varnished with Talens-Rembrandt Picture Varnish matt (probably containing ketone resin) - between **1970 – 1976**,
- 1 painting varnished with MS2A - in 1971
- 6 paintings are varnished with Keton N – in 1980
- + a few with a wax, natural resins (mastics and dammar) and other synthetic resins (Talens Acrylic Varnish (matt/gloss) and Paraloid B 72)

The scarcity and incompleteness of information regarding additives, solvents and descriptions of application in the treatment reports make it difficult to understand the exact usage of these synthetic resins. On some of the affected paintings the AW2 varnish is degraded (yellowing, blanching, cracks and cuppings), while on others it is in good condition.

It is likely that **wax** has been added to the AW2 resin (results ATR-FTIR, literature). Some of the observed visual disturbances might be caused by the added wax.

The ketone resins and in particular **AW2** were proposed as varnish materials due to the need of new, more stable varnish materials (Cleaning Controversy England 1946-1963, seminar on resinous surface coatings in Oberlin Ohio 1959) and their optical and physico-chemical properties that made them desirable with respect to natural resins or other acrylic polymers (which convinced due to stability but felt short in optical properties).

Ketone resins have been used widely since the 1950's due to good film building properties, good optical properties, its good handling properties and solubility in non polar solvents (expected also after ageing). The main additives are: dammar, wax, bleached stand oil, castor oil, industrial plasticisers, can be applied by brush or spray and dissolve in solvents such as turpentine oil and white spirit.

The ageing behaviour is not extensively studied, but it is known that mainly **oxidation** processes take place at carbonyl groups (Norrish I and II reaction), some double bonds, tertiary carbon atoms, hydrogen atoms in alpha-position to carbonyl groups. With increasing oxidation the polarity changes in polarity from non-polar to more polar – just as natural resins and the materials inherited brittleness causes micro cracks and possibly blanching. The information on yellowing in literature is contradictory.

Mock-ups are needed to achieve a better understanding of the behavior of the low viscous and low-molecular weight resin on the painted surface. Of special interest is its penetration into the paint layers with different pigment volume concentration, and the influence this has on the results that can be achieved with analytical tools. Further, the mock-ups will serve to execute preliminary cleaning tests.

Between December 2016 and end of 2018 the research project on AW2 varnishes is developed in **4 stages**:

1. **Internal documentation** on the use of ketone varnishes at the Munch Museum and preliminary analyses using ATR-FTIR spectroscopy for identification of the chemical nature of the coatings present on some paintings. A standardized documentation procedure (standardized condition report, photo-documentation and mapping) is designed. All paintings will be photographed unframed and according to set standards in normal light, raking light and UV radiation (also backside) and microscope images will be taken for all important details. A number of around 23 paintings in the Munch Museum's collection have been documented as being varnished with ketone resins between the 1950s and '80s. These paintings cover the period 1882-1940 (Figure 1).

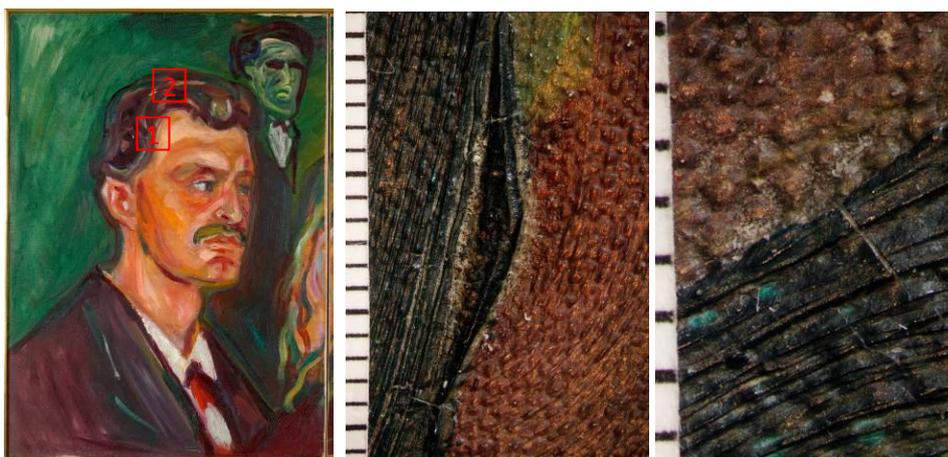


Fig. 1. E. Munch. *Selvportrett mot grønn bakgrunn* (Woll M 645). 1905. 64 × 45.5 cm.

Oil on Easel Painting. Front and detail photographs: detail 1 shows varnish material that accumulated beside pastosity, detail 2 shows blached varnish material that causes a greyish appearance. Photo by Munch museum.

2. **Creation of mock ups** with ketone varnishes using reference materials for comparison with paintings at the Munch Museum and Museum Behnhaus/Drägerhaus in Lübeck. The mockups will also be valuable for completing the database of reference materials at MUM and to better understand the behavior of the varnish layers during cleaning tests (monitoring of the cleaning effectiveness will be possible, using samples and measurement areas on the mock-ups, before and after removal of the varnish). The mock ups were left to age in laboratory environment and part of them were also sent to age artificially for 3 months at RCE, Amsterdam.

3. **Analytical campaign on varnish samples** retrieved from all the paintings under study using several techniques: optical microscopy, microFTIR, GC_MS, Py-GC_MS etc. These analyses will allow to better understand the complex composition of varnish materials (vs. the paint materials beneath) and also to assess their degradation-deterioration pattern.

4. **Establishment of a method for varnish removal** and assessment with analytical tools (colorimetry, microscopy, surface profilometry, SEM-EDX, OCT technique etc.). The literature proposes several materials and methods for removing natural and synthetic coatings from oil paintings [10-11]. However, the challenge is posed when it comes to identify the presence of residues (.e.g. from the varnish material or the medium used for removal) [12]. Therefore, the methodology for assessing the effectiveness of removal has to be complemented with analytical tools [10, 13-14].

Questions addressed by Access:

The access to scientific and documentation archives in the 3 institutions allowed improving the knowledge on the type of ketone coatings, their use in restoration, advantages and disadvantages of their application in practical case studies.

Furthermore, the personal contact with conservators and conservation scientists experienced in modern paintings is valuable for the practical accomplishment of MUM's project. Of particular relevance is the information regarding which cleaning methods have been successfully used, which were the basic requirements during their preparation and which can be the best approach to assess the effectiveness of removal.

The Access helped clarify formulations that were successfully tested in the OPD's and other laboratories and which were the major drawbacks of these cleaning systems. This knowledge will allow us to conduct experiments in the Munch Museum collection. The scientists from the three institutions can also contribute to designing the proper methodology for assessing the effectiveness of varnish removal.

Main objectives of the project proposal:

The Access project's aims are:

- to give an overview on the use of ketone resins varnishes in other collections (where works by Munch or contemporary artists are present) and their experience in subsequent removal;
- to help build a network of specialized contacts with other institutions in Europe which can enhance the knowledge we have on these varnish materials, to establish a methodology for characterizing the chemical nature of coatings present in the selected easel paintings and their degradation patterns;
- to establish the best methodology for removing the degraded ketone coatings;
- to develop an analytical protocol for assessing the effectiveness of the varnish removal, in order to understand which changes occur during cleaning on the painted surface, which is the depth of the cleaning and if there are any residues left from the varnish or cleaning formulation;
- to establish the correct methodology for creating mock ups with multilayered structure and varnish coatings;
- to test and validate the best methodology for assessing the behavior of the varnish layers on mock ups.

The Access to information available at OPD, CATS and RCE on the removal of ketone varnishes and the direct interaction with conservators and scientific staff from these institutions contributed to:

- understand the extent of the use of ketone resin varnishes in other collections and to clarify the lack of knowledge on the ageing and removability of ketone resins
- compare our knowledge (in terms of bibliographical references and methodology) to the one already existing in their archives and laboratories;
- acquire knowledge on already tested cleaning formulations (recipes), their precise composition and effectiveness;
- understand which were the adopted methods and methodology of study of the varnish/painted surfaces during the cleaning with such formulations and their advantages vs. disadvantages;
- understand the limitations of cleaning systems and of monitoring with analytical tools the treatment's effectiveness;
- confront with real case-studies from these institutes current practice the potential and results of the varnish cleaning.

Main achievements of the ARCHLAB visit:

Three different institutions (OPD, RCE and CATS) in 3 different countries (Italy, Netherlands and Denmark) were visited by Irina Sandu and Charlotte Stahmann between May and September 2017 and the achievements of these Access visits can be summarized as following:

1. Analytical databases and documentation;
2. Conservation condition and treatments reports and other related documentation;
3. Mock ups samples and ketone resins of different composition and provenance/provider
4. Access to analytical facilities for artificial ageing and additional characterization of materials (both for mock ups and real samples);
5. Access to libraries and scientific papers of different collections.

1. Analytical databases and documentation

A) At OPD the following data was available on consultation and also copied for internal use of the users from MUM:

- Images of UV induced photography on 2 canvas paintings treated with Laropal K80 mixture;
- Images of cross-sections of the 2 paintings (before the treatment) which were treated with ketone resin varnishes;
- 6 FTIR spectra of ketone resin (Laropal K80?) and of Laropal A81;

A short visit was done at the storage room of the Paintings conservation section to observe under UV radiation a panel painting by Giotto where ketone resin was applied as final varnish (Figure 2).



Madonna col Bambino, Giotto – Vis and UV induced photography (by Pino Zicarelli - Laboratorio Fotografico OPD Firenze)

Fig. 2. Panel painting varnished with Laropal K80 varnish and wax and mock ups with several formulations of varnish (as mixture of ketone resin, mastic and wax in a solvent)

B) 23 analysis reports were received from **RCE** . These reports contain analysis results indicating ketone resin as varnish material, some reports also contain extracts from treatment reports mentioning the application of ketone resins. Scientists from RCE (Henk v. Keulen, responsible for GC-MS and Klaas Jan van den Berg, responsible for DTMS) pointed out the challenges of

identifying ketone resins because they have so many compound peaks and recommended a tailored procedure (right temperature, number of steps) for GC-MS to analyse ketone resins and also the use of DTMS in a comparative study between diterpenoid resins and ketone resins. A discussion about the solubility of the AW2 beads that are in possession of the Munch Museum was carried out pointing that they are still soluble in white spirit after ageing and that the solubility of the beads is not comparable to the one of the varnish. It was also discussed that ketone resins can be found in paint layers, due to penetrated varnish or the presence of ketone resins in paint medium that were added to the paints by artists. A collection of recipes from Talens was checked and Painting Media and Varnishes that have Ketone N and AW2 as an ingredient were found in it.

- C)** The **CATS** have almost no experience with the study on varnish materials. Therefore, they also do not have any analytical reference spectra and no cross-sections of paintings varnished with ketone resins. An UV photography's (E. Munch Summer Evening and Oda Buhre, V. Hammersøi Asiatisk plass) was made available by SMK.

2. Conservation condition and treatments reports and related documentation

- A)** A visit to the Archive of **OPD** in Via degli Alfani in Florence made possible the access to documentation on restoration reports from 6 paintings and also on UV images from 2 canvas paintings.

The restorers from Restoration of paintings lab usually apply the varnish based on ketone resin (Laropal K80) as final varnish over a varnish made of mastic (or Dammar) resin. The proportion of the mixture is 1 p resin: 2 p solvent (white spirit or turpentine oil; if white spirit is used Toluol or acetone is added also) and the application is done by spray.

- B)** The experience of conservators working with **RCE** and as private conservators on the use of ketone resins was illustrated through cases from the practical experience in which a varnish was difficult to remove from the paint layer as it became sticky and didn't dissolve properly, or when the varnish was removed mechanically after increasing the materials brittleness through exposure to solvent via a poultice. Without any analytical proof that the varnish was indeed a ketone resin the nature of the varnishes cannot be confirmed, but the varnish seemed to be synthetic and behaved as described when removed.

The visit at RCE made possible to meet also conservators from outside the institute, such as Anna Krekeler (paintings conservator at the Rijksmuseum), Kathrin Krisch (private working paintings conservator), Oda van Maanen (Van Gogh Museum). They unfortunately have no or little experience with ketone resins.

- C) During the visit at SMK** with Pauline Lehmann Banke and Troels Filtenborg (both paintings conservators) the use of Ketone resins (first AW2, later Ketone-N, followed by MS2A) at the SMK was mentioned. The use of Ketone-N resins varnishes was according to Troels stopped after the IIC Conference in Brussels (1990), both have never used AW2 resin varnishes

themselves (it was used in the generation of conservators before them). They have not noticed any problems with these varnishes so far, but often problems like these are not noticed before someone/something is drawing the attention to it. In general, treatments such as application or removal of varnishes do not have a priority at the SMK and are therefore not often executed. Pauline mentioned the decrease of aromatic compounds used in White Spirits from the mid 1980's to only 0,01 % of aromatic content. A higher aromatic content is not allowed in Denmark. Several folders (including condition and treatment reports – Figure 3) of paintings that have been varnished with AW2 or other ketone resins between the 1950's and 1990's were made available at SMK:

- 28 folders of paintings painted by Munch's early contemporaries from the second half of the 19th century (V. Hammershøi, P.S. Krøyer, V. Johansen, L. Frølich, J.F. Willumsen, T. Philipsen, J. Skoygaard, E. Nielsen, H. Smidth),
- folders of the five paintings by E. Munch (Oda Buhre, 1891), Workers on their Way Home (1814), Death Struggle (1915), Portrait of Daniel Jacobsen, Summer Evening were checked.

Of 28 paintings (from Munch contemporaries) varnished with ketone resins, 20 were varnished with AW2 (1965-1992), 7 with Keton-N (1982-1993), 1 with MS2A (1992). Some of the paintings were checked in the exhibition with UV lamp and in raking light. The varnish was fluorescent on all the paintings without glassing. With the observation only by eye (without microscope) no obvious degradation phenomena could be seen. All the paintings were quite heavily treated before the AW2 resin varnish was applied (i.e. cleaning, removal of previous varnish, lining, and consolidation), it was therefore difficult to clearly distinguish the varnishes inherent properties from materials that were on the surface from other treatments.

Also one of the Munch paintings (Olga Buhre) has been varnished with the ketone resin AW2 in 1968 by Henrik Bjerre, conservator at the SMK at that time. Summer Evening has a very unregularly applied layer of a translucent material. The fluorescence of the material shows that the material probably lays underneath the signature and it was suggested (K. Korbela 2013) that this material has been applied by Munch himself. We can expect that more paintings at the SMK have been varnished with AW2 and other ketone resins; at least 30 folders of paintings that were painted before Munch's time were varnished with ketone resins. Due to a lack of time they were not investigated closely. Scans from SMK's "conservation recipe book" with several recipes containing AW2 were also allowed.

Treatment/condition reports at SMK where ketone varnishes are mentioned



Fig. 3. Documentation consulted during the Access to SMK archive

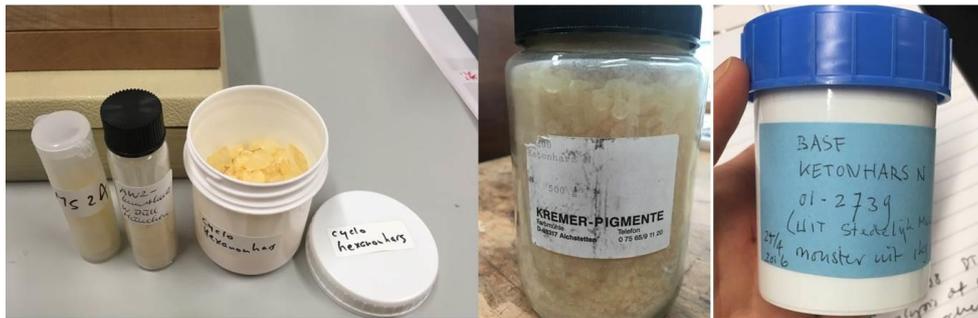
3. Mock ups samples and ketone resins of different composition and provenance/provider

- A) Mock ups** were found by Oriana Sartiani from OPD containing mixtures of varnish materials (mastic + Laropal K80 + wax in different concentrations – Figure 2) and a small quantity of **Laropal K80 resin** from Zecchi (Florence) were also given for analysis and eventually for preparing new mock ups. 5 samples of mixtures of Laropal with mastic and wax from mock ups prepared in 1990 in the Conservation-restoration laboratory and 3 bottles with solutions of already prepared varnishes based on Laropal K80 (Fig. 4) were given.
- B)** Henk Keulen from RCE gave **three samples of reference materials** (ketone resins), they are labelled as follows (unfortunately without production number or date): Cyclohexanone, AW2 from Firma Düll and MS2A. Jan Dorscheid (Rijksmuseum) provided samples of MS2A and Ketonharz-N.
- C)** The SMK has a **large collection of old restoration materials**, several bottles of ready-made varnish materials and unsolved ketone resins in beads were amongst them. A sample of all of them was taken and brought back to the Munch Museum for analysis (Table 1).

Solutions of ketone varnishes from OPD



Ketone resins from RCE, Amsterdam



Collection of old varnishes and ketone resins from SMK, Copenhagen



Fig. 4. Images of the reference materials in the 3 institutions where ketone resins or solutions of varnish were found

Table 1 gives all the samples of ketone resins gathered during the Access in form of beads or bottles with solutions.

4. Access to analytical facilities for artificial ageing and additional characterization of materials

At RCE it was agreed with Klaas Jan that artificial ageing of mock-ups with ketone varnishes can be done for 3 months and DTMS analyses available both for reference and real samples of ketone varnishes. Klaas Jan proposed the methodology of light ageing. Ineke Joosten also expressed availability to collaborate with SEM-EDS analyses of the mock-ups surfaces after the ageing.

5. Access to libraries and scientific papers of different collections

A) Literature consulted at OPD, Florence

- Publications from OPD where final varnishing with ketone resin is reported:
- Paola Bracco, Oriana Sartiani, Caterina Toso, «Per te parte porto». Tecnica artistica, stato di conservazione, e intervento di restauro dei dipinti, in Andrea Mantegna. La Pala di San Zeno. Studio e conservazione, a cura di Marco Ciatti e Paola Marini, Edizioni Edifir Firenze, 2009, p. 125-174;
- OPD Restauro 23, 2011, Ministero per i Beni e le Attività Culturali, Centro Di Firenze, p.155-166;
- La Madonna di S. Giorgio alla Costa di S. Giorgio, Studi e Restauro, a cura di Marco Ciatti e Cecilia Frossinini, Edifir, Firenze, p.80.
- Other papers from IIC collection and OPD restauro.

B) Literature consulted at RCE, Amsterdam

- Dutch conservation journals: KM – kunstenaarsmateriaal.nl, CR 1997-2007, Art Matters
- De Witte: Polycyclohexanone resins
- Recipies Talens (confidential)
- ICOM CC – 12th Triennial Meeting Lyon 29.august – 3. September 1999
- IIC Nederland – mededelingenblad: restoration of a painting by E. Munch p. 8
- Klaas Jan v. d. Berg et. al: Making paint in the 20th century: the Talens Archive

C) Literature consulted at SMK-CATS, Copenhagen

- IIC Preprints of the contributions to the Brussels Congress, 3-7 September 1990
- Kamila Korbela: The investigation and assessment of the structural problems in Edvard Munch's paintings referring to two case studies from the 1910's. Dissertation 2013.

Dissemination:

I plan to prepare a publication in an Int Journal in consortium with the ARCHLAB providers	X (at least 2 papers and a conference oral communication)
I plan to include the results in my thesis	X (master thesis will be done by Charlotte Stahmann at University of Applied Science Cologne)
I have no plans yet	

You are kindly invited to provide pictures that might be used to illustrate the advantages of ARCHLAB to the public.

*:I agree that the content of the ACCESS report is available on the Iperion CH website making sure that copyright issues of the provider are respected.

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9. Robert L. Feller, Catherine W. Bailie: Solubility of Aged Coatings Based on Dammar, Mastic, and Resin AW-2. In: *Bulletin of the American Group of the International Institute for Conservation* (12/2). 1971. pp. 72-81.
10. *New insights into the Cleaning of Paintings.* *Cleaning 2010*, Eds. L. Fuster-López, A. Elena Charola, M.F. Mecklenburg, Ma Teresa Domenéch-Carbo, Preprints of the International Conference organized by Universidad Politecnica de Valencia, Instituto de Restauracion del Patrimonio, Smithsonian Museum Conservation Institute, May 26th-28th 2010, p. 47;
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12. Stulick D., Miller D., Khandekar N., Wolbers R., Carlson J., Peterson W.C., *Solvent gels for the Cleaning of Works of Art. The residue question,* V. Dorge, Ed. Los Angeles: The Getty Conservation Institute, 2004;
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Table 1. List of reference materials received from the 3 institutions

1	“AW2 Kunstharz 1965” (large resin pieces, with uneven surface, more transparent than the other A.W.2 sample – stored in glass vessel)	SMK
2	“A.W.2” (round resin beads – similar to the ones at the MuM – stored in glass vessel)	SMK
3	Resin MS2A, No. 16,345, Date:9.3.70., Laporte Industries Limited, organics & pigments division, Stallingborough Lincolnshire England, red sticker: Ringsted & Semler A7S, Nr. Farimagsgade 13, 1364 Kobenhavn (translucent plastic bag with lable)	SMK
4	“M.S. 2 A” (stored in brown glass vessel)	SMK
5	MS2A-Harz, No. 67240, Harz für hochlichtechte Gemäldefirnisse, Kremer Pigmente (plastic bag with paper label)	SMK
6	MS2A-Harz, No. 67240, Harz für hochlichtechte Gemäldefirnisse, Kremer Pigmente (white cylindrical plastic box with screw lid with paper label, 500 g) underneath the Kremer label another label saying: Linden Chemicals Batch 0705006	SMK
7	Rembrandt picture varnish – Royal Talens, Talens & Zoon N.V. Apeldoorn (original glass bottle - large bottle)	SMK
8	Rembrandt picture varnish for oil paintings– Royal Talens (original glass bottle - small bottle)	SMK
9	Rembrandt varnish mat – Royal Talens (original glass bottle – not very bleached label)	SMK
10	Rembrandt varnish mat – Royal Talens (original glass bottle –middle bleached label)	SMK
11	Rembrandt varnish mat – Royal Talens (original glass bottle - very bleached label)	SMK
12	Van Gogh varnish mat – Talens (original glass bottle)	SMK
13	Okerin, syntetisk voks fra Frank W. Joel, England, prøve fra Bent Hacke	SMK

14	A-voks	SMK
15	n-keeton harpiks (From the universities of Copenhagen's collection probably from the 60/70's (received by David Buti – CATS	CATS
16	Laropal K80 resin from Zecchi (Florence) – beads in a plastic bottle	OPD
17	«Cyclohexanone» (sample received from Henk v. Keulen – material was not stored in the original vessel)	RCE
18	«AW2 from Firma Düll» (sample received from Henk v. Keulen – material was not stored in the original vessel)	RCE
19	MS2A (sample received from Henk v. Keulen – material was not stored in the original vessel)	RCE
20	MS2A-Harz (67240)– Harz für hochlichtechte Gemäldefirnisse – Kremer Pigmente (sample received from Jan Dorscheid – Rijksmuseum - in original bottle)	Rijksmuseum
21	Ketonharz N (??200) – Kremer Pigmente (sample received from Jan Dorscheid – Rijksmuseum - in original bottle)	Rijksmuseum