

Volatile binders

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from Kunsttechnologie II/95

Part I: Applications

Reversibility is a term with a magical ring in the field of modern conservation practice.

Reversibility initially means the reversibility of measures, processes and interventions on an object. The fact that once an intervention has been carried out, it can no longer be undone does not need to be further emphasized. It is rather the changes to the original structure of the object caused by an intervention that can be limited.

In the following, interventions will be described in which substances are introduced into a structure, but also disappear from there again without the structure having been changed as a result.

In this first publication, the emphasis is on the description of the procedures and the materials used. Further applications and detailed investigations on treated objects are being prepared for publication.

However, it should be explicitly stated here that, as is usual with any concept development, material compatibility must be checked in each case.

The basic consideration is based on the idea of temporarily solidifying sensitive objects or protecting them against external influences with a sealing coating, working with substances that are present as solids at a certain temperature but at the same time have a sufficiently high vapor pressure to evaporate.

At the same time they should have the properties

- meltable at a temperature below 65° C
- immiscible with water
- soluble in the usual solvents
- non-toxic and environmentally compatible

In fact, quite a number of substances possess these physical properties.

Over the last two years, a large number of these substances have been tested for applicability in the field of preservation. Of all these, three substances have been selected for further work.

1. cyclododecane, melting point approx. 60° C
2. menthol (D,L), melting point approx. 31-35° C
3. tricyclene-camphene (technical mixture), melting point approx. 35° C

The physical and chemical properties of these substances are discussed in detail in the second part of this paper.

When used for restoration purposes, the volatility is of particular importance. In a practical experiment, the degree of volatility can be estimated in a simple way:

It is the loss of film thickness within 24 h under "normal conditions". This is based on the assumption that the layer evaporates on one side.

- For cyclododecane, this corresponds to approx. 0.03 mm in 24 hrs.
- For menthol this corresponds to approx. 0.04 mm in 24 h.
- For tricyclic camphene this corresponds to approx. 0.4 mm in 24 hrs.

This means that a layer thickness of approx. 1 mm of cyclododecane will have completely disappeared after approx. 33 days with exclusively one-sided evaporation.

With tricyclene-camphene mixtures, this is already the case after a few hours.

Examples for the use of the volatile binders:

Consolidation of materials

Transport securing

Particularly in the case of transport securing, it is important that the materials used for securing are only temporarily effective and that the objects have not undergone any changes after transport.

Japan paper laminations

The classic method for conservators of Japan paper lamination of endangered painting and priming layers on panel paintings and polychrome sculptures can also be carried out in the same way with vb (volatile binders) provided that material compatibility is guaranteed. Since the materials described above have different properties not only in terms of melting points and evaporation time but also in the way they form a film, the material used must be carefully selected. Menthol, for example, is particularly suitable for lamination because of its better adhesive properties.

The time period for which the lamination is planned is also important. The layer thickness of the lamination on the one hand and the evaporation time of the material used on the other hand are decisive here. For example, when using menthol, a layer thickness of approx. 500 μ would be sufficient to ensure stability for two weeks. When using tricyclic-camphene mixture, a layer thickness of 6.6 would be required for the same period.

The procedure is similar to that for waxing: First, a saturated solution of menthol in pentane is prepared. This solution can now either be applied directly to the painting layer surface, and in a second step, Japanese paper is applied and again coated with the menthol solution in pentane.

A drying time of about one hour must be observed. A second option is to iron menthol-soaked Japanese paper directly onto the surface using a heating spatula.

On porous substrates, the following procedures have proved successful: A dense intermediate layer of cyclododecane or menthol is sprayed as a melt onto the areas concerned. This can be covered with Japanese paper and acrylic dispersion. The lamination is removed by simply peeling off the acrylic-Japan paper layer and evaporating the intermediate layer. In sensitive areas, the intermediate layer can also be dissolved with aromatic-free gasoline.

Short-term effective laminations (for a few hours) can be produced with the technical mixture tricyclene-camphene as follows: The melt is spread on the area in question. In a second layer, a reinforcement of glass fiber fabric or gauze is applied and coated with the melt. This type of lamination remains readily deformable.

Other possibilities for transport protection is pre-consolidation in the manner and technique of wax consolidation of loose paint and primer layers.

solidifications - full impregnations

Transport protection for particularly sensitive or already damaged objects can be produced with the aid of impregnation.

(Archaeological excavation finds, etc. are the main objects to be considered here). First of all, it must be decided whether to work with a solution or with the melt.

In my experience, only materials that evaporate very quickly, such as tricyclic-camphene mixture, can be considered for solidification as transport protection.

Otherwise, waiting times until complete evaporation would be too long.

A technically relatively simple method of slowing down the evaporation process is to store the object in a polyethylene bag. The evaporation time can be extended up to twenty times. It would even be conceivable to store the object for an unlimited period by using appropriate packaging. In any case of solidification, it is important to finally produce a layer of fB as thick as possible on the surface.

The procedure: The object is soaked with a saturated solution of tricycles in pentane. If the situation allows, the object is doused or even immersed in the solution. After soaking, wait until the solvent evaporates before storing the object in a polyethylene bag.

Sampling

Sampling for scientific investigations is facilitated, particularly in the case of sensitive materials, by the fact that crumbling is prevented by prior solidification. Again, only materials that evaporate very quickly, such as tricyclic-camphene mixture, come into question.

For the procedure: A heavily salinated, only weakly bonded plaster mortar is to be removed. For this purpose, the removal area is also soaked with a saturated solution of tricyclene in pentane. After soaking, it should be waited until the solvent evaporates.

Another method in which drying times can be omitted is working with the melt.

In this case, however, the area to be soaked with the melt must be heated to a temperature of approx. 40° C using an infrared radiator. Due to its low viscosity, the melt penetrates very well and solidifies into a wax-like mass after cooling.

Consolidations

Great importance have for the consolidation of fragile objects during the period of mechanical interventions.

Mechanical interventions

On wall paintings, the remaining plaster mortar on the backsides should be reduced to a specified layer thickness. For the procedure: The back of the mortar is coated with a saturated solution of menthol in pentane. This procedure can be repeated (after an intermediate drying time of about one hour) as necessary.

Ultrasonic cleaning or powder blasting

Hard overpaint or sintered layers on weakly bonded lime mortar can be thinned out using the powder blasting process. In this case, the weakly bonded lime mortar should be temporarily consolidated to prevent the mortar surface from breaking through during cleaning. Since in this case a strength lasting for several hours (possibly even days) in the layer thickness range of approx. 10 μ must be expected, Cyclododecane is chosen as the strengthening agent. About the procedure: The melt is sprayed onto the surface in question with a heating spray gun at a temperature of approx. 60° C. A waxy coating forms on the surface. This forms a waxy coating on the surface, which is melted in a second operation with an infrared lamp or heating spatula. Care must be taken to ensure that the material is completely absorbed by the substrate. If necessary, residues are removed from the surface with boiling limit petrol.

Bindemittel für Dichtungsmassen und Stützörtel

Vorübergehende Abdichtung von Rissen, Löchern oder Fugen hat im Zusammenhang mit dem Einsatz von Festigungsmitteln oder Injektionsmassen im Wandmalereibereich oder auch in der Steinkonservierung eine grosse Bedeutung. Wichtiges Ziel ist in diesem Zusammenhang, die Dichtungsmasse wieder restlos entfernen zu können, ohne dabei die originale Umgebung zu beschädigen oder zu verändern.

Sealing compounds

The production of the sealing compound depends, of course, first and foremost on the task in hand. A sealing mortar compound that is to be able to close cracks several centimeters wide and initially maintain a pressure of several bar must be designed differently from a sealing compound that has to fulfill this task in the hairline crack area. Basically, only in the area of hairline cracks can the fB melt be used. All other openings require an additive to the binder.

The vb described above, both as melt and as saturated solution, have such a low viscosity that phase separation occurs when mixed with fillers. A simplest way to increase the viscosity is to add highly dispersed silica (Aerosil HDK or Cabosil). The tixotropy created by the addition of HDK also has a favorable effect on the production of mortar masses. As with the examples already described, planning should first be made for the minimum service life of the sealant. For restoration work, this is certainly not much more than the service life or setting time of the consolidant or injection mortar. For such short service lives, a rapidly evaporating vb such as tricyclene-camphene mixture is well suited.

For waterproofing measures on large wall surfaces, as required for masonry grouting, a slow-evaporating binder such as cyclododecane should be used. Should the waterproofing need to be resumed before the final evaporation of the vb, the sealants can be removed very easily with white spirit

Sealing of surfaces

The often necessary protection of sensitive surfaces should not and in most cases must not be permanent. It should be limited above all to the period immediately during an operation.

Hydrophobic coatings

In addition to the mechanical processes already mentioned above, chemical cleaning processes constitute one of the most frequent interventions on porous substrates such as plaster mortars and natural stones. The soluble substances introduced into the structure by the water during these measures form an enormous hazard potential. Temporary, volatile sealing of the substrates in question can considerably reduce the hazards caused by such cleaning processes.

The intended goal of temporary sealing is to keep the surface of the object (approximately 200 to 300 μ layer thickness) open to the aqueous solutions, while sealing the areas immediately below the surface to be waterproof.

About the procedure: Since in this case the greatest importance is attached to consistent layer thickness, the slowly evaporating materials are preferable. The surface of the mural or natural stone is painted with a saturated solution of cyclododecane in pentane. This procedure must be repeated in many cases until a drop of water rolls off the surface evenly.

Protective coatings

Sensitive surfaces are often endangered by construction measures (static fuses, grouting, needling, etc.). Coatings with vb provide protection against all types of contamination (such as paint, spray mist, mortar or cement residue, etc.) without the need for masking.

Protective coatings can consist of all three materials. The selection results from the requirements as already described. Processing is carried out as a melt with the aid of a heating spraying device.

Part II: Materials and material properties

The main requirements placed on substances used in the temporary consolidation or sealing process described in Part I

- conventionally called volatile binders - can be summarized as follows:

- The substances must be solids at room temperature.
- They must have a distinct volatility or high vapor pressure and evaporate within a reasonable time without leaving residues.
- They must be hydrophobic, i.e. water-repellent or non-water-miscible.
- They must be applicable as a melt or as a solution in solvents.
- They must be fundamentally compatible with materials.
- They must be non-toxic and environmentally compatible.

These criteria are met by a number of non-polar organic compounds, primarily from the cyclic hydrocarbon class of substances. These include the substances presented here, cyclododecane (C₁₂H₁₄), camphene and tricyclene (both C₁₀H₁₆), and - with some restrictions - menthol (C₁₀H₂₀O). These substances are characterized by a wax-like solid, tack-free or slightly tacky consistency at room temperature, they have a melting point of about 35-65° C and a boiling point of between 150 and 230° C. Their outstanding property is their clear volatility, i.e. their ability to pass directly from the solid state, i.e. bypassing the liquid state, into the gaseous state, a property which can be equated with sublimation under atmospheric pressure..²

Volatility and vapor pressure

The evaporation rate of a substance, i.e. its volatility below its boiling temperature, is not a readily measurable or theoretically calculable substance constant; it depends on a number of sometimes contradictory factors such as the vapor pressure and the heat of evaporation of the evaporating substance, the external conditions - humidity, ventilation, etc. - as well as interactions with the impregnated structure. - as well as the interactions with the impregnated structure; it cannot be derived from the boiling temperature.³

Every solid or liquid substance releases individual molecules from the molecular compound into the gas space, an equilibrium is established - depending on the temperature. The pressure exerted by the gaseous phase in equilibrium with the solid or liquid substance on the turns of a closed system is defined as the vapor pressure of a substance. The vapor pressure is a specific property of the substance and depends exclusively on the temperature. If the space available to the vapor is reduced (e.g. by covering the surface with film) or increased (e.g. by ventilation), the vapor pressure at a given temperature does not change. Instead, either molecules from the gaseous phase are returned to the solid or liquid phase (if the space is reduced) or further molecules are transferred to the vapor space. The same applies to cooling or heating of the system.

The equilibrium and thus the vapor pressure is determined by the molecular composition and by the sum of the intermolecular forces of attraction that can emanate from the molecules; they determine the heat of evaporation of a substance. Substances with a non-polar structure, such as hydrocarbons, have a higher vapor pressure and thus a higher rate of evaporation than substances with polar structures, given the appropriate molecular size.

The relationships described above are familiar to us for the organic solvents commonly used in restoration, but they apply equally well to solids. Solids can also evaporate if they have a correspondingly high vapor pressure. Naturally, the rate of evaporation of solids will be much lower, but it can be influenced in a controlled manner by heating or by ventilation or by covering, as described above. This is of co-decisive importance for the use of the volatile binders in the various fields of application.

In the evaporation processes described so far, possible interactions with the impregnated microstructure have not been taken into account. According to the investigations of C.M. Hansen⁴, an evaporation process (of solvents) can be broken down into two phases: Phase 1 is determined by the "normal" evaporation factors: Dependence on vapor pressure, heat of evaporation, temperature and pressure, phase 2 is determined by possible interactions with the subsurface, the retention. Retention can be decisive for the evaporation time of a substance, possibly the substance can remain in the porous structure for years. However, if we consider the evaporation of a solvent or a volatile binder from a polar structure, such as a wall painting or a plaster coating, the risk of prolonged retention exists primarily with substances of higher polarity, but not with non-polar hydrocarbons, such as those used here. Longer retention with possibly negative consequences - e.g. persistent hydrophobicity - should therefore be ruled out with the volatile binders described here.

Complete evaporation of a volatile substance is only guaranteed if it is free from impurities. For this reason, it is essential to ensure that only compounds of high purity are used. If compounds are to be used that can change under unfavorable conditions and there is therefore a risk of residues forming, i.e. compounds of low volatility, these may only be used in a very weak form, e.g. provided with antioxidants. This could possibly apply to the use of camphene or menthol, both of which seem to be ideal for this process due to their physical properties, but at the same time may show a certain reactivity, acid or oxidation sensitivity, respectively, based on their molecular structure (cf. description of the substances in the appendix).

Solubility of the volatile binders

The volatile binders are soluble in non-polar solvents such as saturated or aromatic hydrocarbons, in halogenated hydrocarbons and ethers. With solvents of medium polarity, such as esters, they show low solubility. They are almost insoluble in ethanol and acetone. They are not miscible with water.

The insensitivity of the volatile binders to both water and polar solvents allows a wide range of applications from cleaning with aqueous and non-aqueous systems to preservation measures with the various manufacturing systems.

Application options - melt or solution

The volatile binders are applied in molten form, usually to the preheated substrate or dissolved in a suitable solvent. In a number of applications of this process, such as lamination, transport protection, etc., the volatile binders are applied in excess to be on the safe side.

In other cases, e.g. when cleaning water-sensitive surfaces or partial cleaning, the binder must be applied very selectively and its evaporation rate controlled. In this case, the volatile binders will be used in dissolved form, since this allows them to be applied in uniform layer thickness.

The penetration capacity of the binder melt is strongly dependent on the ambient temperature: only when the substrate is preheated can the volatile binder penetrate sufficiently deeply. The viscosity of the melt is very low for the volatile binders, so that they can penetrate well in most cases; migration will usually not occur if the treated surface cools quickly and the binder solidifies. Care should be taken not to overheat the binders, otherwise there is a risk of material alteration, not to mention the not inconsiderable flammability of some substances (see below).

The penetration capacity of the binder solution is influenced by the properties of the solvent and by the viscosity and surface tension of the solution.

In principle, structural penetration is problematic because the volatile binders, like their solvents, have only a low surface tension due to their nonpolar molecular structure, but the higher the surface tension, the greater the penetration depth. If necessary, the procedure described by Domasłowski for structural consolidation using solvent mixtures with a fast-volatile "good" solvent and a slow-volatile "bad" solvent can also be used successfully here⁵. If, for example, only near-surface impregnation is required, i.e. migration of the binders to the surface is desired, a highly volatile solvent, such as pentane, can be used without further ado.

Film Education

It is important for the success of the process that the volatile binders form a solid film in a suitable manner when cooling below the melting point or after evaporation of a solvent. The type of film formation is crucial: only substances that form a film that is as dense as possible can seal the surface in such a way that the apposition of e.g. aqueous media is possible and no penetration into the sealed sections takes place. If the substance forms a layer consisting of many separate individual crystals, e.g. when using unsuitable solvents or excessively diluted solutions, it is unsuitable.

Toxicity and environmental compatibility

The volatile binders should have as little or no toxic effect as possible, so that trouble-free use can be ensured. In selecting the substances tested for use in this process, strict attention was paid to ensuring that - when handled properly - they do not pose any risk to health or the environment.

In the case of volatile binders and, above all, low-boiling organic solvents, there is the problem of high flammability or explosion hazard in enclosed, inadequately ventilated rooms.

Since special precautions are always necessary here, tests with other flammable but environmentally compatible solvents are currently in progress.

It should be emphasized again at this point that the applications of the process described so far concentrate on areas of conservation where interactions with the non-polar organic binders are not to be expected. However, if surfaces are to be treated with the extremely solvent-sensitive paint layers, coatings or adhesives, it is essential to carry out compatibility tests beforehand. This applies in particular to the application of the process to paintings, painted sculptures, polished furniture surfaces, etc.. Even without these areas, numerous applications are proposed; they are currently being intensively worked on and prepared for publication, as are examples of applications in the field of paper and textile restoration or the restoration of glass and metal.

Description of each product

From the range of suitable compounds tested up to this point, a few selected substances will be described here. As part of the development of this system, further substances are being tested, especially for special applications. Of the substances presented here, two belong to the group of very volatile substances (camphene and tricyclene) and are thus particularly suitable for short-term consolidation, while the other two substances (cyclododecane and menthol) have a lower evaporation rate and are thus suitable for longer consolidation or hydrophobization.

- Cyclododecane / as spray can
 - Tricyclene-Camphene mixture
 - menthol
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Notes

1. in this context may be a comparison between the long-chain hydrocarbons, the kerosenes and the ring-shaped hydrocarbons, the cycloparaffins. While the open-chain kerosenes with a chain length of C10-C15 are liquids with a melting point of $< 10^{\circ} \text{C}$ and boiling temperatures between 170 and 250°C , the cyclic compounds of comparable molecular size are solid at room temperature. Kerosenes are waxy solid only from a C-number < 20 . However, these are no longer vaporizable without decomposition under normal pressure. One explanation for this phenomenon lies in the molecular structure of the kerosenes or cycloparaffins: at room temperature, the long-chain kerosenes are free-moving in their molecular structure; only at low temperatures do these movements "freeze", and the molecules now have the opportunity to adhere to one another and thus reach a solid state. The ring-shaped cycloparaffins, with their "spherical" more compact shape, have a much higher "freezing" temperature due to the restricted degrees of freedom, and are in a solid state at room temperature.

2. Further examples of substances subliming under atmospheric pressure are p-dichlorobenzene, naphthalene or camphor, which are known to be used as mothballs or powders because of these properties, or a number of aromatic compounds. Due to their toxicity, these substances are unsuitable for use as volatile binders.

3. In practice, it has proved expedient to indicate the volatility (of solvents) by relative numerical values, the evaporation figures. These values are obtained by experimental comparison of the evaporation times of certain quantities of solvents under the same external conditions. The evaporation figures of the "volatile binders" are not



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given in the literature, but they will be many times higher than those of the usual solvents. The values for volatility empirically determined by Hans-Michael Hangleiter for this special field of application via the decrease in layer thickness per unit of time (cf. Part I) show very clearly the typical properties of these substances, but they do not take into account the dependence of the vapor pressure on external conditions such as temperature and pressure.

4. C.M. Hansen quoted after L. Masschelein. Kleiner "Les Solvants cours de Conservation 2" IRPA Brussels 1981 bz.
5. W. Domaslowski, The Mechanism of Polymer Migration in Porous Stones. Wiener Beiträge über Naturwissenschaft in der Kunst, vol.4/5, 1987/88, pp. 402-425.