4.2. Studies in cleaning plastics

4.2.1. Introduction

The approach taken to research into cleaning was to investigate the effect of cleaning thoroughly and quantitatively where possible. Most published studies describing conservation cleaning employ only qualitative evaluation of cleaning techniques. Taking a more quantitative approach involved the development, application and evaluation of new techniques.

Publications and informal inquiries from the year 2000 to date concerning industrial and conservation cleaning were used to select the cleaning materials and aqueous cleaning agents, documented as the most effective at removing soil without inducing measurable changes to the plastic substrate. In the case of solvents and chemical treatments, those that have been considered by conservators as high risk and used, especially by private collectors, but without evaluation were selected. Cleaning materials were evaluated initially for their ability to change or damage model plastics when used alone (mechanical cleaning). Any cleaning materials found to measurably damage model plastics were removed from the study and were not evaluated further.

Those cleaning materials which did not measurably damage clean model plastics were used to apply aqueous, solvent and chemical cleaning agents to model plastics. Agents were rejected if they measurably damaged model plastics. Cleaning materials and agents which caused no measurable damage to clean model plastics were tested for their effectiveness to remove standard soils from model plastics.

Selected model plastics were subjected to artificial light ageing after cleaning in order to predict whether the cleaning process accelerated their degradation. Artificial light ageing was conducted using Xenotest equipment which is thought to simulate and accelerate natural weathering and induce those degradation reactions which take place in real time but within a convenient period. Partners from the Cultural Heritage Agency of the Netherlands (RCE) contributed their extensive experience with xenotesting and their knowledge of the relationship between accelerated ageing periods and real time.

Finally, cleaning methods which had proved the least damaging to plastics and the most effective at removing soil were applied to real objects. The partner institutions took different approaches to cleaning real objects. Some chose to clean a research object, while others cleaned registered museum objects in collaboration with conservators in an attempt to understand how results would be interpreted by people who had not been involved in POPART research.

There was insufficient time in the project to both investigate the effect of cleaning thoroughly and to examine all possible plastic types. The effect of cleaning was therefore examined on the six plastics judged by all partners to be in most urgent need of cleaning in their institutes. Commercially available, uncoloured and transparent cellulose acetate (CA), high density polyethylene (HDPE), high impact polystyrene (HIPS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and expanded polystyrene (XPS) were selected as model plastics to exclude the influence of fillers and pigments on cleaning. The commercial availability of the model plastics used will allow others to extend or repeat the present research. All plastics were supplied as 0.3 cm thick sheet except for CA (0.04 cm) films. PMMA and HIPS films were supplied with protective films on both sides to prevent abrasion and soiling during transport. Protective films were only removed immediately prior to cleaning. Cleaning was conducted on the same side of each model plastic, since initial testing had revealed minor differences in gloss and contact angle between the two sides.

Details of the model plastics are as follows:

- Clarifoil®, cellulose acetate (CA), supplied by DAKA BV, www.daka-oss.com
- PE-HD 500, high density polyethylene (HDPE), supplied by Weber Métaux et Plastiques, www.weber-france.com
- Styrolux 80/20, high impact polystyrene (HIPS), supplied by Bay Plastics Ltd., www.bayplastics.co.uk
- Plexiglas®XT 0A000, poly(methyl methacrylate) (PMMA), supplied by Rias A/S, www.rias.dk

- Transparent oilcloth, poly(vinyl chloride) (PVC), supplied by Jysk A/S, www.jysk.com
- Foam board, expanded polystyrene (XPS), supplied by W Hobby Wholesale Ltd., www.hobby.uk.com

Because CA was included as a model plastic later than the others, not all of the cleaning materials were applied to it during the mechanical cleaning tests. The ten cleaning materials applied were those which had caused least damage to the other five plastics. XPS was cleaned mechanically but then excluded from the project because it proved difficult to see or measure changes on the uneven, inhomogeneous surfaces of the foam.

Model plastics were cut to sizes 4.5 cm x 13 cm or 4.5 cm x 6.5 cm to fit accelerated ageing equipment. Depending on sample size, one or two areas measuring 3 cm x 4 cm were marked on each plastic. Test areas were centred to avoid unevenness or stress at the cut edges.

Artificial ageing of selected model plastics

The light ageing apparatus used for Xenotesting was an Alpha High Energy from Atlas® (ATLAS materials Testing Technology B.V.) fitted with lamp NXE 2000 HE art nr. 56075921. One half of each sample was exposed for 160 hours which represented approximately 40 years real time in a museum environment at 200 lux based on partner RCE's experience. The other half was not exposed. Samples were evaluated visually and change in gloss and contact angles were recorded before and after accelerated ageing.

Evaluation of cleaning

All samples which had been cleaned mechanically or in combination with aqueous, solvent- or chemical-based cleaning agents were evaluated for visual appearance, percentage area scratched, change in contact angle and change in gloss. The effect of cleaning soil from samples was evaluated by visual examination only. Calculations performed for PMMA and PVC suggested that quantitative determinations of percentage area scratched, change in contact angle and change in gloss after cleaning fitted well changes in visual appearance that were judged qualitatively.

Visual appearance

Visual appearance before and after cleaning was used particularly to determine whether the process had either introduced scratches or deposited residues. The cleaned area of the model plastic was compared to a non-cleaned surface of the same plastic. Types of change were recorded.

Percentage area scratched

The percentage of area covered with scratches was calculated for each type of plastic and cleaning procedure. Photomicrographs of surfaces at 25 times magnification were examined for scratches and coloured falsely using the image manipulation program Adobe® Photoshop® at a line width of two units. Images were converted to black and white with Image-J free computer software (www.rsbweb.nih.gov/ij) and the binary threshold feature used to calculate the percentage area scratched. The process was repeated in two areas and an average value calculated.

The inhomogeneous surface structure of XPS made it impossible to measure scratches reliably. Shallow scratches on the PVC film disappeared as they filled with migrating plasticiser.

Change in contact angle

Contact angle gives information about the surface energy (tension) and the polarity of a material. Surface tension is defined as the force per unit length exerted by a surface. Contact angle is the angle a drop of liquid makes with a solid surface. It's magnitude is controlled by the competition between the adhesive forces in the liquid at the surface and the solid plastic which cause the drop to spread across the surface and the cohesive forces between liquid molecules which cause the droplet to form a ball. The contact angle is specific for any given system. If the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid such as paper) the droplet will completely spread across the solid surface and the contact angle will be close to 0°. Less strongly hydrophilic solids will have a contact angle up to 90°. If the solid surface is hydrophobic, the contact angle will be greater than 90°.

Surface tension is affected by the cleanliness and physical structure of surfaces. Contamination increases surface tension which results in a reduced contact angle compared to an otherwise identical but clean surface. Changes in surface energies of model plastics induced by cleaning were likely to be caused either by contamination from residues of cleaning agents or by surface damage such as scratches. They were quantified using changes in contact angle formed between a droplet of distilled water and surfaces of model plastics. Water (20 µl) was applied by syringe and a simple, low cost Veho VMS-004 Discovery Deluxe USB microscope, used at 400 times magnification was used to photograph the process. Contact angles were determined by analysing photographs with the Micro Capture software supplied with the USB microscope. Contact angles were made in triplicate and the mean angle calculated.

It was soon discovered that static electricity induced by cleaning, interfered with contact angle measurements, especially on HIPS and XPS. PMMA remained static for 90 minutes, PVC for 3 hours, HIPS for 24 hours and XPS for weeks. To minimise the influence of static electricity developed during cleaning on the contact angle, particularly on HIPS and XPS, measurements were made more than 24 hours after cleaning. Nevertheless, when studying the calculations, static electricity persisted in XPS as changes were greater for this plastic than the others.

Change in gloss

Gloss of test substrates before and after cleaning was determined using a Minolta multi-gloss 268 reflectometer or similar instrument. It is recommended by the manufacturer that poorly reflective surfaces are examined at 85°, semi-glossy surfaces should be examined at 60° and highly reflective surfaces at 20° (Minolta 2009).

Because the test substrates were transparent and therefore likely to exhibit multiple reflections from internal surfaces, a grey, matt card was placed directly under them in an attempt to reduce extraneous reflections. For PMMA, PVC, HIPS and CA all gloss measurements on new test substrates were greater than 100 gloss units which was attributed to the presence of multiple reflections in the bulk of the plastics. The grey matt card was replaced with both black and white cards in an attempt to reduce reflection from the lower surfaces, but with no measurable effect.

For the two opaque plastics, HDPE and XPS, all gloss measurements on new substrates were lower than 100 gloss units. The standard deviation between measurements was calculated from the percentage gloss determined at 20 different positions on a new plastic films and sheets. For all plastics except PVC the error was found to be ±2 gloss units. After cleaning of each test area, three repeat measurements were made and the mean calculated. 60° gloss was used in calculations because it showed lower variance than 20° and 85°.

Quantifying the effect of cleaning on model plastics-mechanical cleaning vector, M

The many results of percentage area scratched, percentage contact angle change and percentage gloss change were too unwieldy to interpret separately. They were therefore summarised and averaged using a vector. Calculation of the vector required the assumption that there was an additive relationship between percentage area scratched, percentage contact angle change and percentage gloss change. The mechanical cleaning vector, M, was defined as the square root of the sum of the three variables squared. The higher the vector's value, the more damaging the cleaning.

$$M = \sqrt{(\%\text{ area scratched})^2 + (\%\text{ change in contact angle})^2 + (\%\text{ change in gloss})^2}$$

Vector M does not take into account the results of visual examination. A satisfactory way to quantify visual analysis and thereby incorporate them in the vector could not be agreed on by all POPART partners because of the subjective nature of vision. The vector for XPS was not calculated because percentage area scratched could not be measured reliably.

4.2.2. Mechanical cleaning

Twenty three commercially available brushes, sponges, cloths, feathers and compressed gas complied with health and safety requirements, were available in all nine partner countries and were therefore evaluated in the study (Figure 1).

Poly(vinyl acetate) (PVAc) sponge was not used in initial mechanical cleaning tests as the sponge is hard when dry. The sponge was added, when cleaning materials were tested in combination with solvents and aqueous cleaning products.

Although one research group investigating conservation cleaning of acrylic paintings has employed a cleaning machine to standardize the force applied when cleaning with several materials, all other publications describe qualitative attempts to apply repeatable pressures by conservators (Ormsby and Phenix 2009, 2) The POPART project attempted to quantify the force applied when cleaning by applying materials to a model plastic placed on a top pan balance and recording the weight applied. Preliminary trials showed that weights varied from 10 g for brushes and dusters to 40 g for cloths and sponges with an error of ±10 g. Because the measurements were unstable and because the actual area of the cleaning material

Material	Product name	Description	Material	Supplier
Akapad sponge, white	Akapad white no. 4151 (Formerly known as Wishab)	Scouring pad with synthetic sponge. Recommended for conservation of paper	Styrene butadiene rubber	Akachemie Albert Kauderer GmbH, www.akachemie.de
Akapad sponge, yellow	Akapad hard no. 4121 (Formerly known as Wishab)	Scouring pad with synthetic sponge. Recommended for conservation of wall paintings	Synthetic rubber	Akachemie Albert Kauderer GmbH, www.akachemie.de
Canned air	Pressurised Air Duster	Can containing 400ml	Compressed air	Lyreco Danmark A/S, www. lyreco.dk
Compressed air	Compressed air	Compressed air from a pressure line. Technically cleaned for oil residues		
Cotton bud	Cotton Wool Hospital Quality code 5909	500g roll. Homemade cotton bud made on a china stick	Cellulose	Robinson Healthcare Ltd., www.robinsoncare.com
Cotton cloth	Dish towel	Woven cotton. Washed before used	Cotton	SuperBrugsen, www.superbrugsen.dk
Duzzit sponge	Duzzit sponge eraser	Package with four sponges in blue and white	Melamine formaldehyde resin	151 Products Ltd., www.151.co.uk
Feather duster	Feather duster	A single feather obtained	Ostrich feather	Handler textiler, www.handler-textiler.dk
Goat hair brush	Japanese brush	Size 2 (width 50mm)	Goat hair	Deffner und Johann GmbH, www.deffner-johann.de
Latex sponge	Make-up sponge	Bag with 20 sponges in white and skin colour	Latex	Netto Supermarket, www.netto.co.uk
Leather chamois	Leather chamois	Washed before use. Soft (fluffy) side was used for testing	Tanned lambskin	Stiwex/ DAY-system A/S, www.day-system.com
Lens paper	Assistent Linsenpapier no. 1019	Package with 500 sheets	Cellulose	Assistent Glaswarenfabrik Karl Hecht GmbH & Co, www.hecht-assistent.com
Microfibre cloth	Microfibre cloth	Thick fibres and open weaving	Polyester and polyamide	EverClean, www.brauner-as.dk
Paper cloth	Tork Premium Multipurpose Cloth 510 Roll	Roll with 1000 sheets	Cellulose pulp, polypropylene and polyester fibres	SCA Hygiene Products A/S, www.tork.dk
Paper tissue	Tork Premium Facial Tissue Extra Soft	Package with 100 sheets	Virgin fibres (cellulose)	SCA Hygiene Products A/S, www.tork.dk
PVA sponge	Spezialschwamm "Blitz fix"	175 x 75 x 35 mm	Polyvinyl acetate-based sponge	Deffner und Johann GmbH, www.deffner-johann.de
Sable hair brush	A&B brush no. 6074	Size 8	Sable hair	A & B pensler, www.bottzauw.dk
Scotch-Brite sponge	Scotch-Brite® Non-Scratch Scrub Sponge no. 625	Scouring pad with soft sponge	Polyurethane ester	3M, www.3m.com
Spectacles cloth	Spectacles cloth	Thin fibres and closed weaving	Polyester and polyamide	EverClean, www.brauner-as.dk
Synthetic feather duster	Swiffer Duster Kit	Synthetic feather duster	Polyester and polypropylene microfibres	Swiffer®, www.swiffer.com
Synthetic leather chamois	Synthetic leather chamois	Synthetic chamois with small holes	Viscose and synthetic latex	Anton Walraf Söhne GmbH & Co, www.walraf.com
Synthetic rubber sponge	Make-up sponge (synthetic)	Bag with 40 sponges in white and pink	Styrene butadiene rubber	M-cosmetics, www.matas.dk
Tooth brush	Tooth brush	Soft hairs	Nylon hair	Unknown origin
Dry-ice	Asco Carbon Dioxide	Temperature of solid CO_2: 79°C	Solid carbon dioxide	LTL Dry Ice APS, www.ltl-dryice.dk

Figure 1. Cleaning materials evaluated

excluding air pockets in contact with the surface is required in any calculations of force, quantification was deemed too complex to employ. Instead, all mechanical cleaning of all model plastics were performed by the same person. The aqueous and solvent cleaning of each individual plastic was executed by the same person.

From both literature and discussion with conservators it was clear that mechanical action was most often applied either in linear or circular directions and therefore both were investigated. Five linear rubs were applied to the upper half of each model plastic with each cleaning material and five circular rubs to the lower half. When cleaning with canned air the instruction on the can was followed. The can was held upright and air was sprayed in short bursts for around 30 seconds. A similar procedure was used for the application of air from a pressure line. To prevent contamination, samples were placed in a covered box immediately after cleaning.

Dry ice (solid carbon dioxide) was one of the mechanical techniques evaluated. Carbon dioxide as snow at -79° C was applied to all model plastics except for CA via a spray pistol attached to a compressor. Dry ice sublimes on making contact with surfaces leaving surfaces dry immediately after cleaning. The process was carried out by an experienced operator from the company LTL Dry Ice APS (www.ltl-dryice.dk).

Visual appearance

Scratches were more visible on HIPS and HDPE than on the other model plastics. Duzzit and Scotch Brite sponges and all paper based products caused scratching. Residues were only visible on PMMA, but this was mainly due to the transparency of the material. CA, PVC and XPS showed no changes visible with the naked eye. For PVC this was probably due to plasticisers present at surfaces, which made the plastic appear slightly opaque. Surfaces of HDPE and HIPS had matte and pitted appearances after cleaning with carbon dioxide. XPS was completely destroyed by the treatment. No visible changes were present on PMMA and PVC.

Percentage area scratched

Microscopic examination showed that all cleaning products scratched surfaces with the exception of canned and compressed air. This finding counteracted the general perception by conservators and other museum professionals that mechanical cleaning is a non damaging technique to remove soiling from plastics.

Some plastics were more readily scratched than others. The most sensitive was HIPS followed by HDPE, PVC, PMMA and CA. Duzzit sponge induced the highest percentage area scratched than any other material tested. Scotch Brite sponge, synthetic leather chamois and all paper based products also caused more scratching than the average cleaning material. Area scratched and depth of scratches were significant factors affecting scratch visibility. When more than 3% of a surface area was scratched deeply, as shown by applying a nylon bristled toothbrush, damage was visible to the naked eye. If scratches were shallow, they were only visible when more than 10% of the area was affected.

When examining surfaces for scratches an interesting phenomenon was noticed on plasticised PVC. The plastic scratched easily, but with time the film repaired itself, as plasticiser migrated to surfaces and filled scratches. This was particularly noticeable on samples which had undergone accelerated ageing. Here the initial scratches were invisible after ageing. After the phenomenon was discovered, a standard procedure of always measuring scratches within two days after cleaning was implemented.

Change in contact angle

Change in contact angles induced by cleaning revealed that both types of Akapad sponges, air from an in-house compressor, latex and synthetic rubber sponge induced great changes. As these materials did not scratch surfaces more than the average cleaning material, change in contact angles was attributed to deposited residues. Cleaning with Duzzit and Scotch Brite sponges also changed contact angles, but this was attributed to the high concentration of scratches. Within the conservation world it has often been discussed whether synthetic feather dusters leave residues on surfaces. No changes in contact angle were determined in the current research.

Changes in gloss

In general, changes in gloss induced by cleaning were measurably lower than changes due to scratching and changes in contact angle. Duzzit sponge was the only cleaning material which greatly reduced gloss. HIPS and PVC were more sensitive to gloss changes than the other model plastics. For PVC this may be attributed to folds or deformations induced in the flexible film by cleaning. No measurable changes in gloss were measured on CA, PMMA and XPS.

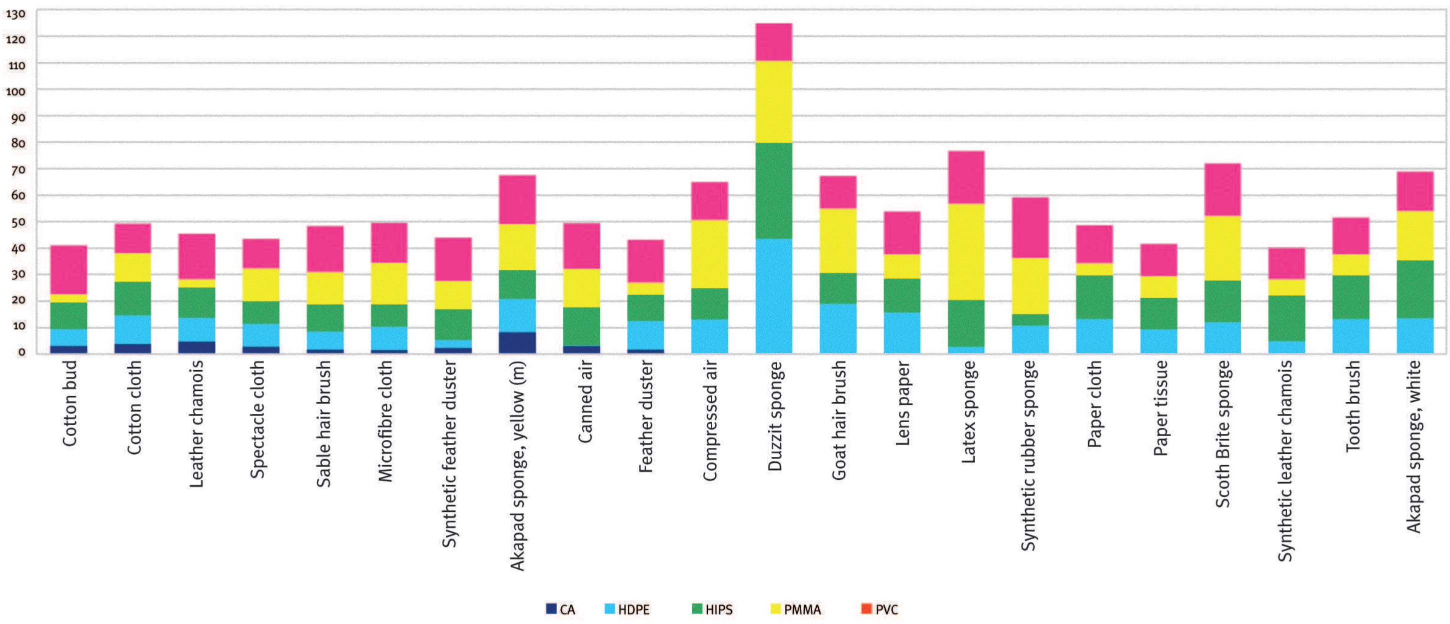

Figure 2. Addition of mechanical cleaning vectors for CA, HDPE, HIPS, PMMA and PVC

Mechanical cleaning vector, M

Percentage area scratched, percentage contact angle change and percentage gloss change were summarized using vector M. The vector suggested (Figure 2) that all cleaning materials induced changes to plastic surfaces, although not all were visible with the naked eye. Based on experience and observation of mechanical cleaning of plastics, it was decided that cleaning materials with a mechanical cleaning vector greater than 50 could not be recommended for cleaning. The most damaging materials were Duzzit-, Latex-, Scotch Brite and both Akapad sponges. The least damaging cleaning materials listed in order of most harmless first were synthetic leather chamois, cotton bud, paper tissue, feather duster, spectacles cloth, synthetic feather duster, leather chamois, sable hair brush, paper cloth, cotton cloth, canned air and microfibre cloth.

Initially, change in contact angle and change in gloss were studied separately. As scratches were considered to be irreversible forms of damage, a low percentage area scratched was prioritized in evaluating cleaning materials. Duzzit and Scotch Brite sponges and all paper based products including lens paper, paper cloth and tissue scratched surfaces. Basing results on scratching alone, suggested that the cleaning materials which caused least damage to surfaces were canned air, cotton bud, cotton cloth, feather duster, leather chamois, microfibre cloth, sable hair brush, spectacles cloth, synthetic feather duster and yellow Akapad sponge.

On calculating the mechanical cleaning vector, the yellow Akapad sponge gave a value higher than the proposed limit of 50 mainly due to the residue deposited on surfaces by the sponge. In retrospect, had the cleaning vector been introduced earlier in the project, the Akapad sponge would not have been selected to subsequently apply aqueous, solvent and chemical cleaning agents.

No visual differences were recorded when aged mechanically cleaned samples were compared to aged non-cleaned plastic. After ageing, gloss and contact angle reduced equally for all plastics before and after cleaning.

4.2.2. Aqueous cleaning

The practice of aqueous cleaning comprises both dissolving dirt and removing it physically from surfaces. In the POPART project, aqueous cleaning agents were applied using the least damaging materials from the mechanical cleaning evaluation. These materials were cotton bud, cotton cloth, leather chamois, microfibre cloth, sable hair brush, spectacles cloth, synthetic feather duster and yellow Akapad sponge. Despite a good performance in mechanical cleaning tests, feather duster could not be used in combination with aqueous cleaning products simply because the feathers collapsed when wet. Canned air was not used in combination with aqueous cleaning products, as blowing liquid from surfaces was considered an unrealistic cleaning technique. Poly(vinyl acetate) (PVAC) sponge was added. The sponge had not been tested in the mechanical cleaning tests, because it is completely hard when dry.

The aqueous cleaning agents evaluated were:

- Dehypon LS45, 1% (w/w) in distilled water, non-ionic detergent, cloud point 22°C, fatty alcohol C12-C14, experimental critical micelle composition (CMC) 0.0598 g/l, supplied by Conservation Resources Ltd. (UK), www.conservationresources.com
- Distilled water
- Judith Hofenk de Graaff detergent, 1% (w/w) of concentrate in distilled water, non-ionic detergent, concentrate comprises 50 g sodium dodecylbenzenesulphonate, 50 g tri-sodium citrate and 5 g sodium carboxymethylcellulose in 1000 ml distilled water, concentrate prepared by partners RCE
- Orvus WA Paste, 1% (w/w) in distilled water, anionic detergent sodium lauryl sulfate. Orvus WA paste has an experimental CMC of 0.29 g/l, supplied by University Products. The Archival Company® (US), www.universityproducts.com

- Synthetic saliva, used as supplied, mucin (35mg per ml), unspecified quantities of xylitol, methylparaben, dinatrium, benzalkoniumchloride and EDTA, supplied by Pharmachemie BV (NL), www.tevapharmachemie.com
- Triammonium citrate (TAC), 2.5% (w/w) in distilled water, supplied by VWR & Bie & Berntsen, www.vwr.com

Model plastics were cleaned as supplied when new, to examine which aqueous cleaning techniques, if any, induced measurable changes to the plastics themselves. The least damaging aqueous techniques were subsequently applied to plastics after application of standard soils to investigate how effective they were at removing dirt. XPS was excluded from further cleaning because it proved too difficult to measure changes.

It was concluded from mechanical cleaning that any dust or dirt present on surfaces was more effectively removed when applying the material in five linear rather than circular rubs. Scratching was also minimised. All plastics were cleaned with all possible combinations of the nine selected materials and the six aqueous agents. After cleaning, surfaces were rinsed with distilled water and another five rubs with the same material.

In an attempt to optimise experimental reproducibility, it was decided that 1 ml of each cleaning agent would be applied to each cleaning material. However, this was not practical. The volume of cleaning agent absorbed or supported by cleaning materials depended on both composition and dimensions. Instead it was decided to apply the cleaning agents to each material and then squeeze or press any excess out. This method better represented real practice because materials were moist and not wet. After cleaning, plastics were placed face up and allowed to dry for 24 hours at 18-22°C and 40-60% relative humidity. To prevent accumulation of dust, plastic samples were placed in a covered box immediately after cleaning.

All cleaned areas were examined for four different properties, namely appearance, percentage area covered by scratches, change in contact angle and change in gloss. As described for mechanical cleaning in section 4.2.1, gloss measurements, contact angle and percentage of surface scratched were quantified and summarized as a vector; the higher the vector the more damaging the cleaning agent/material combination.

After cleaning new plastics, sable hair brush, synthetic feather duster and yellow Akapad sponge were deemed damaging because they deposited residues on surfaces, which were difficult to remove by rinsing. As a result, they were not evaluated for cleaning soiled plastics.

Two standard soils used by other cleaning researchers to model fingerprints (sebum soil) and carbonaceous soil (organic oil soil) were prepared from published recipes (Kuisma *et al.* 2005; Koponen *et al.* 2007). Sebum soil was prepared by dissolving palmitic acid in 1-propanol and stirred magnetically while covered for 15 minutes to produce a 20% concentration. Organic oil soil was prepared by adding carbon black in the form of very fine bone black pigment to paraffin oil in the ratio 5:95 by weight and mixed by magnetic stirrer for 60 minutes. It was used immediately. Dirt was applied by dropping 0.05 ml of organic oil soil or 0.03 ml of sebum soil onto a template with an opening to the model plastic of 3 cm x 4 cm and spreading using a bar coater. As paraffin oil is non-drying, it formed a very greasy and mobile film on surfaces. To dry the organic oil soil, samples were placed in a warm (40°C), fan assisted oven for 7 days. Heating reduced but did not remove tackiness. This procedure was unnecessary for sebum soil.

Six aqueous cleaning agents were tested for their ability to remove soil using the six remaining materials. Cleaning was performed with 5 linear rubs. Rinsing comprised 5 rubs with distilled water to remove excess cleaning product. The effectiveness of aqueous cleaning agents on soiled samples was determined by visual examination alone because the soil was found to readily contaminate microscope, camera and reflectometer.

Aqueous cleaning of CA

Compared with mechanical cleaning, it was clear that the addition of aqueous cleaning agents reduced the area scratched by a factor of 10 to less than 0.1%, suggesting that cleaning agents also lubricated plastics. Cotton-, microfibre- and spectacles cloths and cotton bud were the least damaging materials for aqueous cleaning (Figure 3). Akapad sponge was significantly worse, followed by synthetic feather duster and sable hair brush. They performed poorly leaving residues of cleaning agent which changed gloss and contact angle. Excluding the poor results obtained with Akapad, cleaning with Judith Hofenk de Graaff detergent resulted in the least damage, followed by distilled water and Dehypon LS45. Synthetic saliva and tri-ammonium citrate induced greater changes to CA surfaces.

All the aqueous agents demonstrated a good ability to remove organic oil soil, except distilled water which was only partially successful. None of the cleaning agents were effective at removing sebum soil although Dehypon LS45 and Judith Hofenk de Graaff

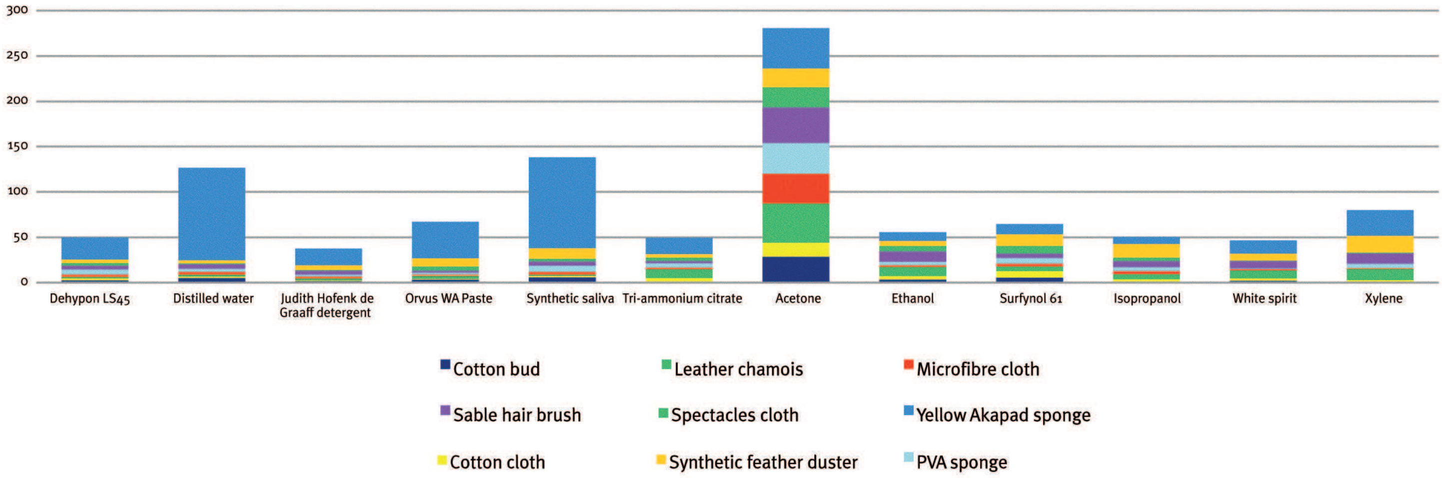

Figure 3. Aqueous and solvent cleaning vectors for clean, unsoiled CA

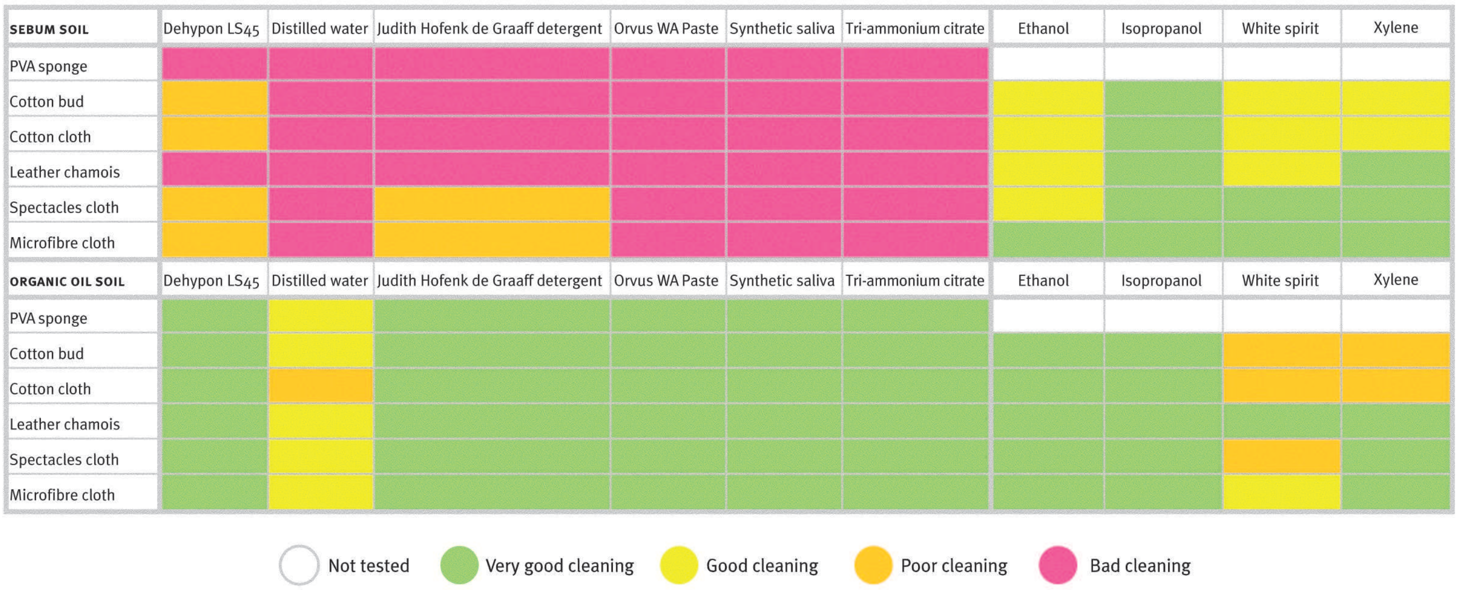

Figure 4. Visual examination of soiled CA after cleaning

detergent partially removed it (Figure 4). During cleaning, it was observed that the microfibre and spectacles cloths were slightly more effective in removing both standard soils than the other materials. Leather chamois often left solid residues on CA surfaces.

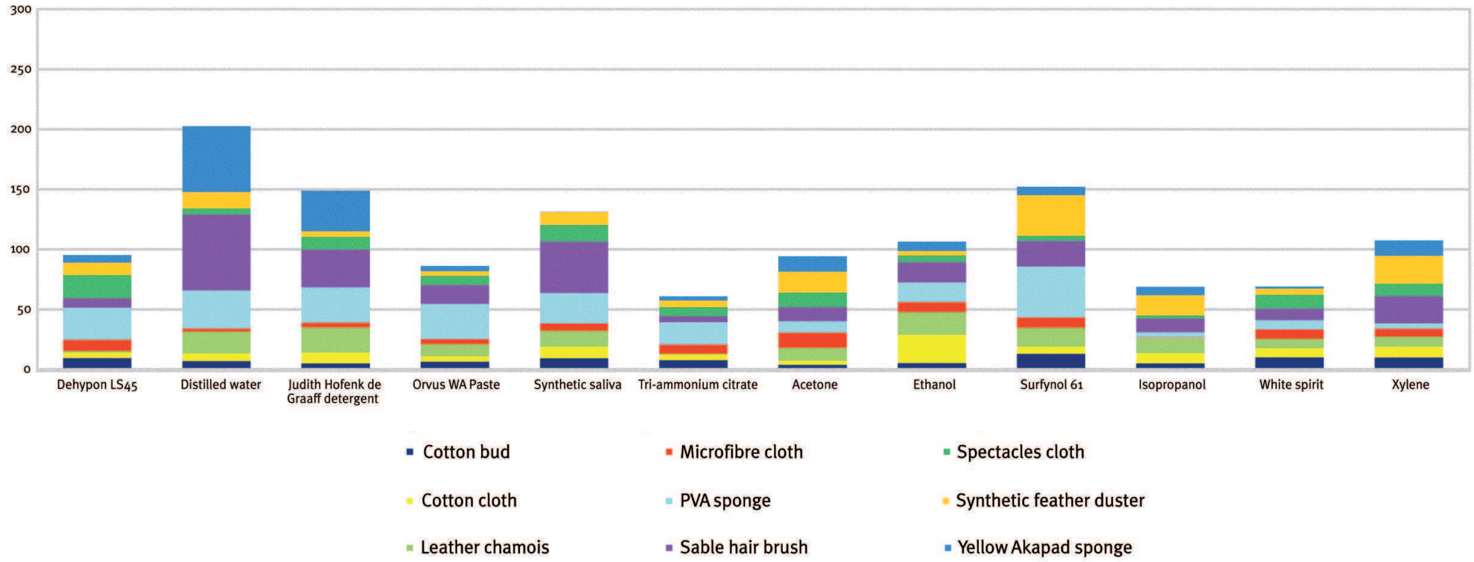

Figure 5. Aqueous and solvent cleaning vectors for unsoiled HDPE

Aqueous cleaning of HDPE

Compared with findings from mechanical cleaning, the presence of aqueous cleaning agents reduced the area scratched by a factor of around 15 to less than 0.1%, suggesting that cleaning agents also acted as lubricating agents for HDPE (Figure 5). Based on cleaning vectors, tri-ammonium citrate was the least damaging aqueous cleaning agent for HDPE while Orvus WA Paste and Dehypon LS45 also showed good results. Distilled water induced most damage to HDPE, probably because it lacked a lubricating agent.

Cotton bud, microfibre-, spectacles- and cotton-cloths were the least damaging materials for cleaning HDPE. Although leather chamois was only slightly damaging to HDPE, residues of leather remained on surfaces even after rinsing. The most damaging cleaning materials were sable hair brush and polyvinyl acetate sponge.

Both types of soil were removed from HDPE by Dehypon LS45 while distilled water and Judith Hofenk de Graaff detergent were poorly effective (Figure 6). Orvus WA Paste, synthetic saliva and tri-ammonium citrate were poorly effective at removing sebum soil. Saliva was effective, however, at removing organic soil. Microfibre- and cotton-cloths were slightly more effective than the other materials tested at removing both soils. Cotton cloth also showed good results when cleaning sebum soiled surfaces and cotton bud was effective for organic oil soiled samples.

SEBUM SOIL	Dehypon LS45	Distilled water	Judith Hofenk de Graaff detergent	Orvus WA Paste	Synthetic saliva	Tri-ammonium citrate	Ethanol	Isopropanol	White spirit	Xylene
PVA sponge	Very good cleaning	Bad cleaning	Bad cleaning	Bad cleaning	Poor cleaning	Bad cleaning	Not tested	Not tested	Not tested	Not tested
Cotton bud	Very good cleaning	Bad cleaning	Bad cleaning	Poor cleaning	Poor cleaning	Bad cleaning	Very good cleaning *	Very good cleaning *	Very good cleaning *	Very good cleaning *
Cotton cloth	Very good cleaning	Good cleaning	Poor cleaning	Poor cleaning	Good cleaning	Good cleaning	Very good cleaning *	Good cleaning *	Very good cleaning *	Very good cleaning *
Leather chamois	Very good cleaning	Poor cleaning	Bad cleaning	Poor cleaning	Poor cleaning	Poor cleaning	Good cleaning	Very good cleaning	Good cleaning	Very good cleaning *
Spectacles cloth	Very good cleaning	Good cleaning	Good cleaning	Poor cleaning	Poor cleaning	Good cleaning	Very good cleaning	Good cleaning	Very good cleaning	Very good cleaning
Microfibre cloth	Very good cleaning	Good cleaning	Very good cleaning	Good cleaning	Good cleaning	Good cleaning	Good cleaning	Very good cleaning	Very good cleaning	Very good cleaning
ORGANIC OIL SOIL	**Dehypon LS45**	**Distilled water**	**Judith Hofenk de Graaff detergent**	**Orvus WA Paste**	**Synthetic saliva**	**Tri-ammonium citrate**	**Ethanol**	**Isopropanol**	**White spirit**	**Xylene**
PVA sponge	Very good cleaning	Bad cleaning	Good cleaning	Good cleaning	Very good cleaning	Poor cleaning	Not tested	Not tested	Not tested	Not tested
Cotton bud	Very good cleaning	Bad cleaning	Good cleaning	Very good cleaning	Very good cleaning	Good cleaning	Bad cleaning *	Poor cleaning *	Poor cleaning *	Very good cleaning
Cotton cloth	Very good cleaning	Bad cleaning	Bad cleaning	Poor cleaning	Very good cleaning	Very good cleaning	Bad cleaning *	Poor cleaning *	Poor cleaning *	Very good cleaning
Leather chamois	Very good cleaning	Poor cleaning	Poor cleaning	Poor cleaning	Very good cleaning	Very good cleaning	Poor cleaning	Very good cleaning	Very good cleaning	Very good cleaning
Spectacles cloth	Good cleaning	Bad cleaning	Bad cleaning	Poor cleaning	Poor cleaning	Good cleaning	Poor cleaning	Poor cleaning	Very good cleaning	Bad cleaning *
Microfibre cloth	Very good cleaning	Poor cleaning	Bad cleaning	Very good cleaning	Good cleaning	Poor cleaning	Bad cleaning	Bad cleaning	Very good cleaning	Bad cleaning *

Not tested · Very good cleaning · Good cleaning · Poor cleaning · Bad cleaning · * Surfaced scratched

Figure 6. Visual examination of soiled HDPE after cleaning

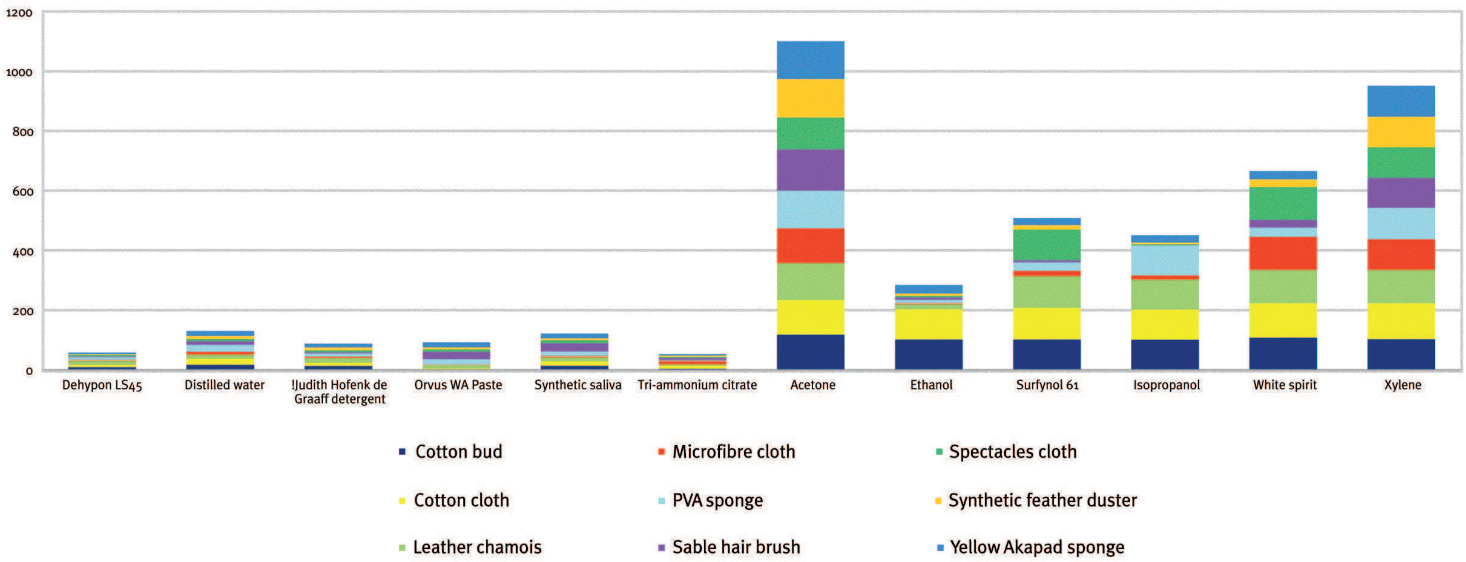

Figure 7. Aqueous and solvent cleaning vectors for unsoiled HIPS

Aqueous cleaning of HIPS

The fact that the presence of aqueous cleaning agents reduced the area scratched by a factor of 35 to around 0.15% compared with mechanical cleaning alone, suggested that cleaning agents also lubricated HIPS (Figure 7). It should be noted that the range of cleaning vector values for HIPS was greater than for the other model plastics and as a result the scale on Figure 7 is from 0 to 1200 compared with 0 to 300 for the other plastics. Tri-ammonium citrate and Dehypon LS45 damaged HIPS least while distilled water and synthetic saliva induced the most changes. Microfibre and spectacles

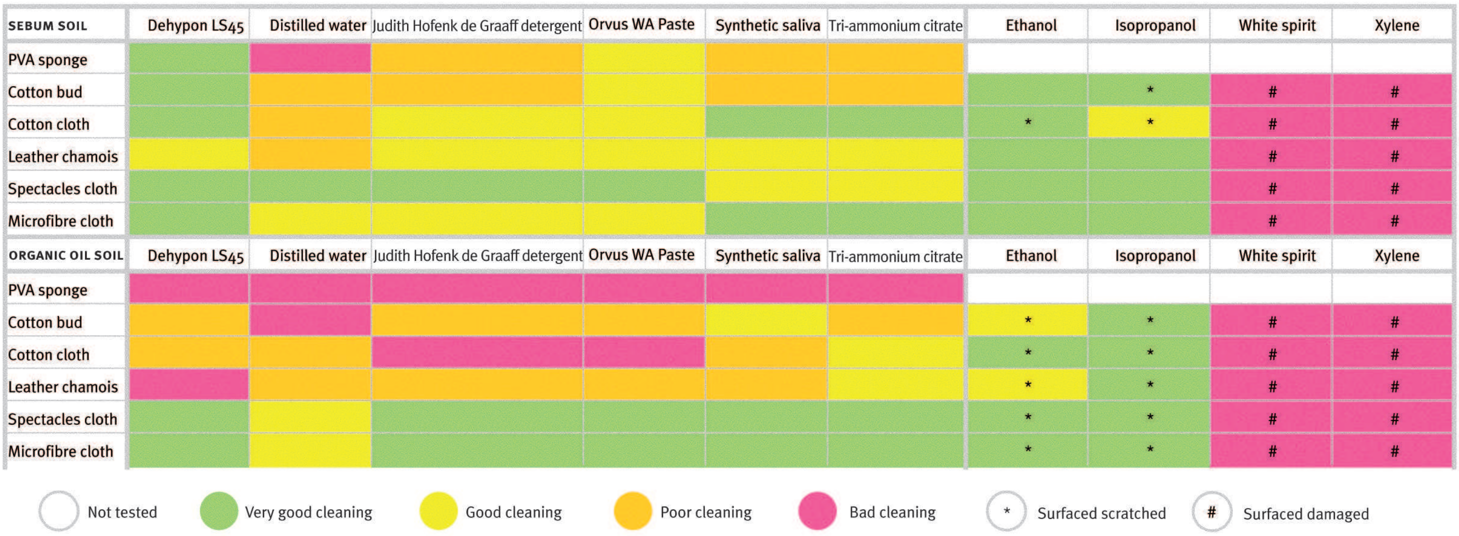

Figure 8. Visual examination of soiled HIPS after cleaning

cloths were the least damaging materials while sable hair brush and PVA sponge damaged HIPS most. Akapad sponge left residues on samples.

HIPS absorbed paraffin oil from organic oil soil and became distorted. Carbon black particles remained at surfaces. Dehypon LS45 was the most efficient agent at removing sebum soil, followed by Orvus WA Paste (Figure 8). Distilled water was poorly effective. None of the aqueous agents were effective at removing organic oil soil. For both soils, microfibre and spectacles cloths were more effective than the other materials tested. Cotton cloth was effective when cleaning sebum soiled surfaces and cotton bud was effective for organic oil soiled samples.

Aqueous cleaning of PMMA

Aqueous cleaning agents reduced the area scratched by a factor of 10 to less than 0.1% compared with mechanical cleaning alone, suggesting that cleaning agents also lubricated PMMA. Orvus WA Paste induced fewest changes to PMMA of all aqueous cleaning agents tested (Figure 9). Distilled water and tri-ammonium citrate induced high levels of scratching because they were less effective as lubricants than detergents. Microfibre-, spectacles- and cotton-cloths were the least damaging materials for cleaning PMMA. Visual examination of samples after aqueous cleaning showed that synthetic saliva could not be removed completely from PMMA by rinsing. Accelerated ageing caused a reduction in gloss and surface energy for PMMA both before and after cleaning. Residues deposited by cleaning did not worsen with ageing.

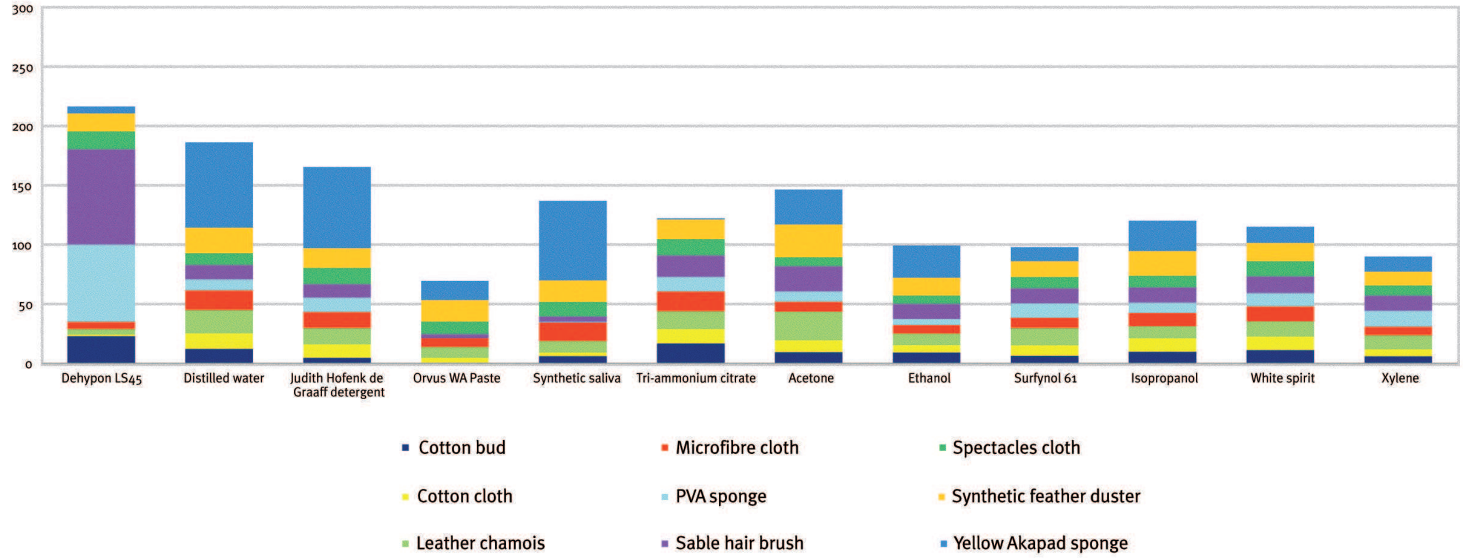

Figure 9. Aqueous and solvent cleaning vectors for unsoiled PMMA

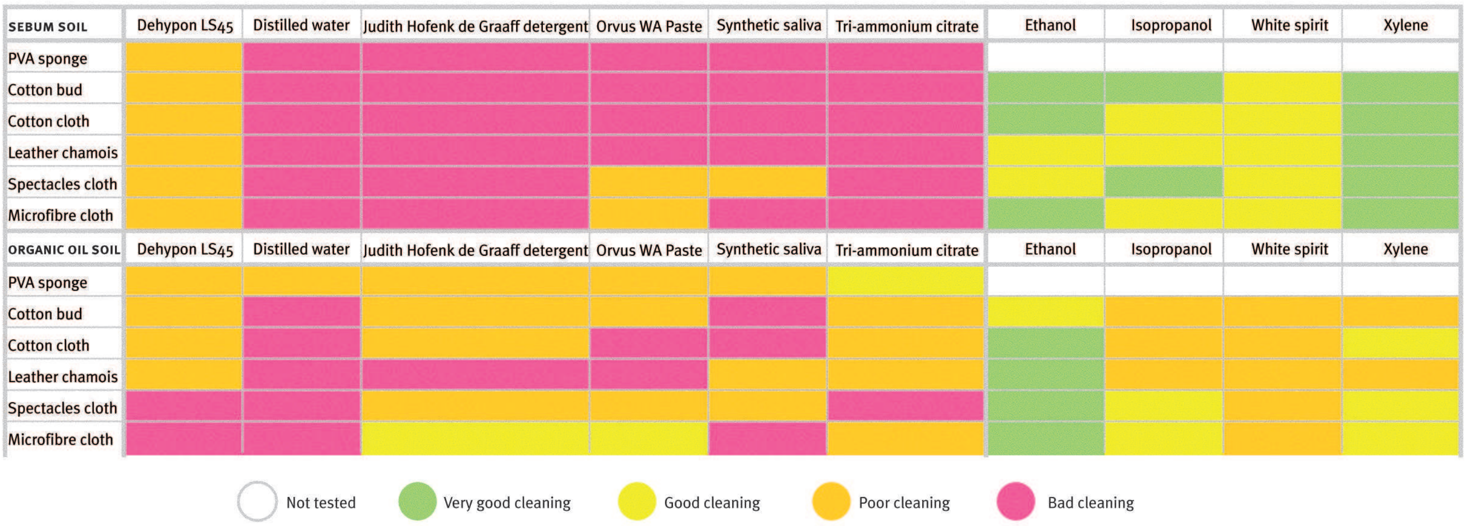

Figure 10. Visual examination of soiled PMMA after cleaning

Dehypon LS45 partially dissolved sebum soil (Figure 10). Distilled water, Judith Hofenk de Graaff detergent and tri-ammonium citrate were ineffective at dissolving the soil. Organic oil was partially dissolved by Judith Hofenk de Graaff detergent, tri-ammonium citrate and Orvus WA Paste. However, none of the aqueous cleaning agents were able to remove soil completely. Distilled water was ineffective. For both soil types, microfibre and spectacles cloths were slightly more effective than the other materials tested. This is most likely because the synthetic cloths are able to hold more soil, due to their greater surface areas to volume ratios. Poly(vinyl acetate) sponge also showed promising results when used for cleaning organic oil soil.

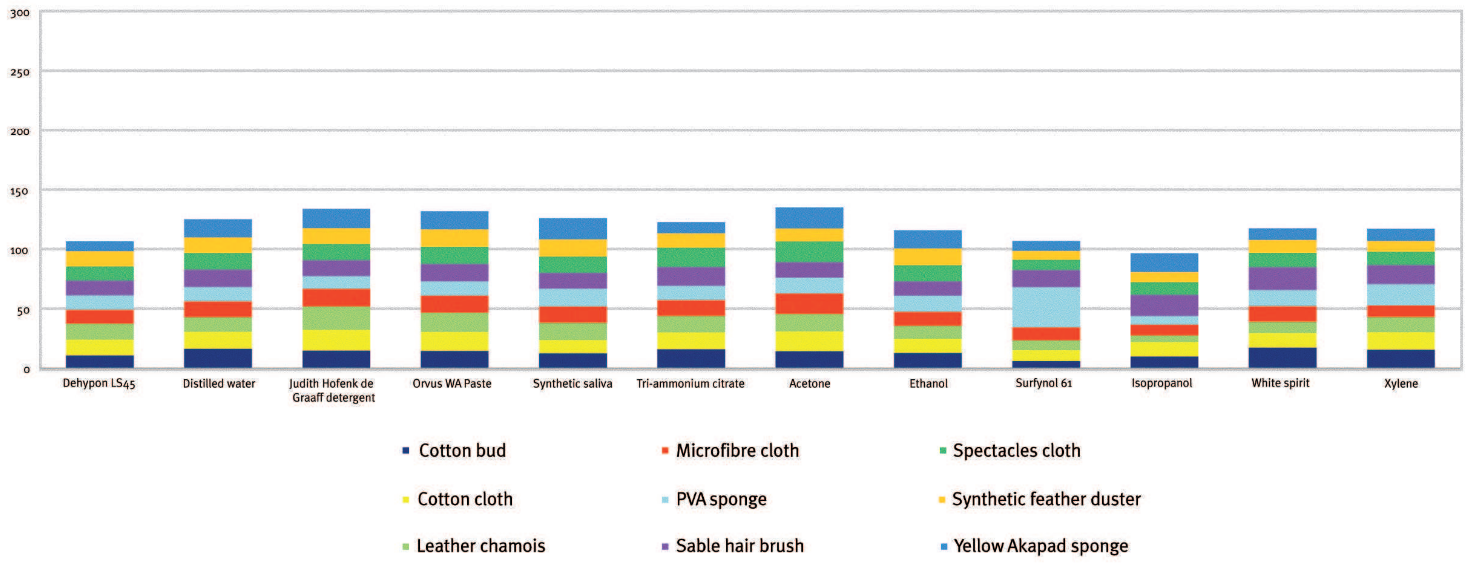

Figure 11. Aqueous and solvent cleaning vectors for unsoiled PVC

Aqueous cleaning of PVC

All combinations of aqueous cleaning agents and cleaning materials produced cleaning vectors with similar values, perhaps because all removed plasticiser at surfaces thus inducing changes in surface energies and gloss (Figure 11). Only yellow Akapad sponges induced changes in appearance. Cleaning with Dehypon LS45 resulted in the smallest changes in surfaces while the application of Judith Hofenk de Graff detergent showed the greatest changes. Scratching of surfaces was reduced by a factor of 5 in the presence of aqueous media compared with mechanical cleaning. Less than 1% of the cleaned area was scratched.

Sable hair brushes transferred dirt readily between surfaces. Photomicrographs revealed that dust particles had accumulated on the hairs which, in turn, scratched surfaces. This observation emphasises that when cleaning plastics it is important to always use clean sable hair brushes and replace them often to avoid transferring soil. Disposable cleaning materials including cloths and cotton bud are preferred. No visual differences between cleaned and non-cleaned PVC on ageing were apparent. Aged PVC underwent similar reductions in gloss and surface energy to new PVC.

Applying soil to PVC using a bar coater was not possible because the films were uneven and crinkled. Instead, 0.1 ml of organic oil soil was applied to the centre of the sample and spread using a glass spatula to cover an area 3 cm x 4 cm. A clean sheet of PVC was then placed on top of the soiled sheet and the organic oil soil massaged into the sheets before peeling them apart. Sebum soil (0.03 ml) was applied to the centre of an area 3 cm x 4 cm. Soil was distributed

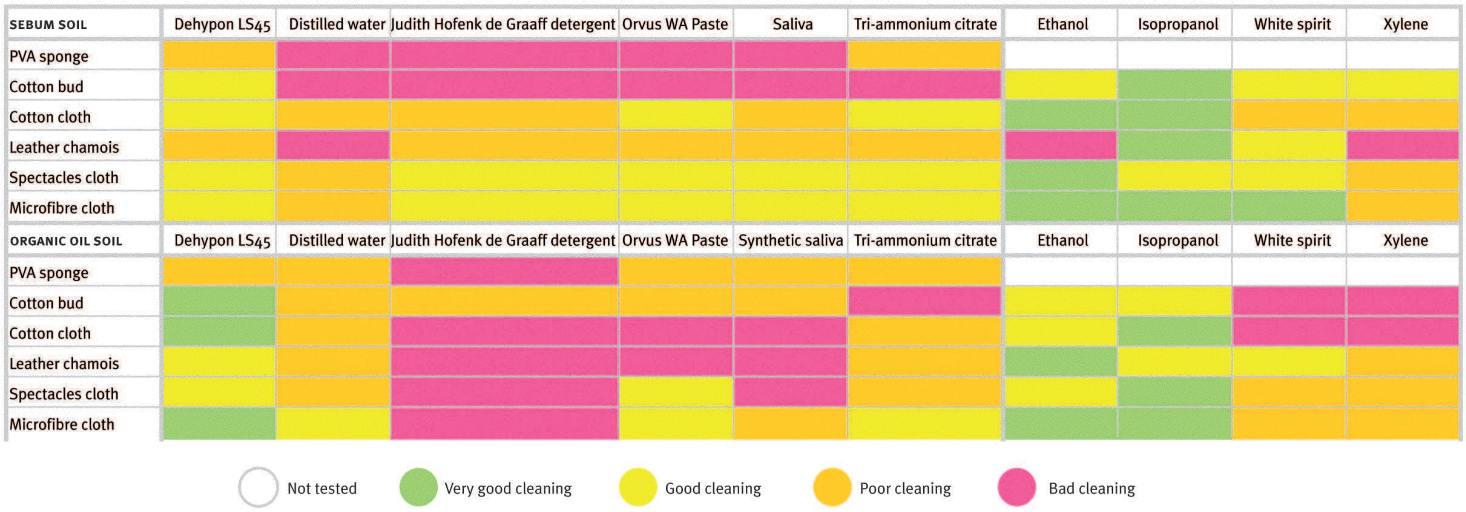

Figure 12. Visual examination of soiled PVC after cleaning

using the rounded end of a sterile glass stick. Soiled PVC was allowed to dry for one week in a covered box at room temperature prior to evaluation. Within weeks of application, soil started to migrate into the film. Sebum soil was less visible at surfaces within a few weeks of application. Organic oil soil had induced severe deformation of the PVC film attributed to migration of paraffin oil into the plastic.

These observations indicated the necessity of cleaning a soiled plastic object as soon as dirt is applied. Sebum soil in particular was more difficult to remove from PVC, compared with cleaning PMMA where soil remained at surfaces (Figure 12). None of the aqueous cleaning agents removed sufficient sebum soil to an invisible level although Dehypon LS45 proved most effective and distilled water least. Organic oil soil was removed using Dehypon LS45 while Judith Hofenk de Graaff detergent and synthetic saliva were ineffective.

Microfibre and spectacle cloths removed more of both soil types from PVC more effectively than the other materials tested. This may be attributed to the fact that the synthetic cloths trapped more soil, due to their greater surface areas to volume ratios. Cotton cloth was effective when cleaning sebum soiled surfaces and cotton bud was effective for removing organic oil soil from PVC.

4.2.3. Solvent cleaning

Experimental setup for solvent cleaning was similar to that for aqueous cleaning. The nine materials used to apply solvents were poly(vinyl acetate) sponge, cotton bud, cotton cloth, leather chamois, spectacles cloth, sable hair brush, microfibre cloth, synthetic feather duster and yellow Akapad sponge. The six solvents were acetone, ethanol, isopropanol, white spirit (a mixture of saturated aliphatic and alicyclic C7 to C12 hydrocarbons with a maximum content of 25% of C7 to C12 alkyl aromatic hydrocarbons), xylene, Surfynol 61 (acetylenic alcohol, 3,5-dimethyl-1-hexyn-3-ol supplied by Kremer Pigmente GmbH & Co, http://www.kremer-pigmente.de).

In addition to the organic solvents, new samples of HDPE, HIPS, PMMA, PVC and XPS but not CA were also cleaned with supercritical CO_2 – a solvent which is increasingly being used as an alternative to tetrachloroethylene (otherwise known as perchloroethylene) in the dry cleaning industry. Carbon dioxide is known either as a gas or frozen in the form of dry ice. When pressure and temperature exceed the critical values for carbon dioxide (31.1°C at 7.39 MPa), it is possible to reach a state where carbon dioxide is still a gas, but with the properties of a liquid. Model plastics were packed inside nylon stockings so that they would not be lost inside the drum of a large washing machine and sent off to company Kymi Rens in Aalborg, Denmark (http://www.kymi.dk). Each sample was visually examined before and after cleaning. Changes in gloss and contact angles were measured. Percentage area scratched was not determined because it was uncertain whether the cause of scratching was the mechanical action of the machine or the carbon dioxide. As a result, a cleaning vector was not calculated.

Solvents were applied using five linear rubs. Rinsing was not necessary as solvents were allowed to evaporate. When cleaning with aqueous agents, except distilled water, surfaces were rubbed ten times (five to clean and five to rinse). This difference in application was considered when comparing results.

Solvents were applied to cleaning materials and excess solvent squeezed or pressed out before application to model plastics. After cleaning, samples were allowed to dry for 24 hours at room temperature and approximately 50% relative humidity, face up, before evaluating. Samples were stored inside a box immediately after drying to protect them from contamination.

Each cleaned area was examined for the four different properties of appearance, percentage area covered by scratches, change in contact angle and change in gloss. As described for mechanical cleaning in section 4.2.1, gloss measurements, contact angle and percentage of surface scratched were quantified and summarized using a vector; the higher the vector the more damaging the solvent/material combination. The effectiveness of solvents on soiled samples was determined visually.

Four materials were deemed unsuitable for cleaning in combination with solvents, namely poly(vinyl acetate) sponge, sable hair brush, synthetic feather duster and yellow Akapad sponge. All left deposits on plastics, were damaged by contact with solvents or proved to be ineffective. Acetone and Surfynol 61 when used as supplied were found unsuitable for cleaning plastics. Contact between acetone and HIPS, PMMA and CA resulted in dissolution or stress cracking of these plastics. Due to rapid evaporation at ambient temperature, acetone's ability to dissolve dirt and lubricate plastic surfaces during cleaning were poor and resulted in a high percentage area scratched, similar to that produced by mechanical cleaning. Surfynol 61 when used as supplied at concentrations greater than 0.1% in distilled water, left deposits at surfaces on evaporation.

Solvent cleaning of CA

Acetone was the most damaging solvent tested, because it dissolved CA. The combination of white spirit, xylene or isopropanol with a cleaning material slightly reduced scratching of CA surfaces compared to applying a cleaning material dry. On visual examination, ethanol gave a similar result to the other solvents except when applied by cotton bud. Acetone and Surfynol 61 increased the percentage of area scratched.

Cleaning vectors showed that acetone induced the greatest change to CA surfaces followed by xylene and Surfynol 61 whereas white spirit was the least damaging solvent (Figure 3). The changes indicated by cleaning vectors were also confirmed by visual examination in the case of acetone and Surfynol 61. Surfynol 61 caused partial dissolution, manifested by blurring surfaces, whereas xylene did not.

Akapad sponge gave the highest vector, followed by sable hair brush, synthetic feather duster and leather chamois. Akapad sponge, sable hair brush and synthetic feather duster, as already mentioned in the results of aqueous cleaning, are not suitable cleaning materials when combined with a liquid agent. Leather chamois left residues only visible by microscopy.

Poly(vinyl acetate) sponge swells or dissolves in contact with solvents resulting in an unsuitable material for solvent cleaning. Cotton cloth, followed closely by spectacles cloth, cotton bud and microfibre cloth were less damaging materials according to cleaning vectors.

For removing standard soils, solvents were more effective than aqueous agents (Figure 4). For removing sebum soil, isopropanol was the most effective followed by xylene, white spirit and ethanol.

The best results in removing organic oil soil were obtained with ethanol and isopropanol.

Although all cleaning materials performed well at solvent cleaning in removing soils, microfibre cloth was slightly more efficient due to its better capacity to absorb the dissolved soil from the CA surface. Leather chamois was shown to be effective but, as already mentioned, leaves solid residues on surfaces.

Solvent cleaning of HDPE

Compared to mechanical treatments, adding solvents Surfynol 61, ethanol, acetone and white spirit to a cleaning material reduced scratching by a factor of four while isopropanol and xylene had no influence.

Cleaning vectors showed that isopropanol and white spirit caused least damage to HDPE (Figure 5). Ethanol applied using spectacle and microfibre cloths imparted little damage. Surfynol 61 damaged HDPE more than other solvents evaluated, particularly when applied by poly(vinyl acetate) sponge, synthetic feather duster or sable hair brush. This could be explained by the fact that Surfynol 61 tended to swell poly(vinyl acetate) sponge and because larger quantities of cleaning agent were applied to surfaces with using synthetic feather duster and sable hair brush. Microfibre and spectacles cloths were the least damaging cleaning materials. Most damaging were synthetic feather duster, sable hair brush and poly(vinyl acetate) sponge. Cotton bud and cotton cloth caused visible scratches. Akapad sponge often left residues and tidelines on surfaces. Poly(vinyl acetate) sponge induced visible scratches in combination with ethanol and isopropanol because the solvents evaporated rapidly and therefore were ineffective as lubricants. HDPE discoloured after cleaning with supercritical carbon dioxide. The colour change was considered unacceptable for a museum object. Its contact angle and gloss were not measurably changed by the treatment.

Solvents were notably more effective than aqueous agents at removing sebum soil but no more efficient for organic oil soil (Figure 6). Both types of soil were removed most effectively with xylene and white spirit while ethanol was the least effective. Although cotton bud was the most effective material for cleaning sebum oil soil, it scratched surfaces. Microfibre and spectacles cloths were less effective but did not induce any visible damage. Chamois leather showed to be slightly less effective than all materials. Organic oil soil was removed most effectively using leather chamois and least effectively by microfibre cloth.

Solvent cleaning of HIPS

Adding Surfynol 61, ethanol, isopropanol and white spirit to a cleaning material increased scratching up to a factor of eight. Damage types ranged from surface dissolution with acetone to dissolution and distortion with xylene. The surfaces of samples cleaned with these two solvents were so damaged that percentage scratches could not be determined and were therefore considered as 100% scratched in cleaning vector calculations (Figure 7).

Acetone was considered the most damaging solvent. It dissolved HIPS resulting in a reduction of gloss of 70%. Surfaces of HIPS cleaned with xylene were dissolved but retained their gloss. Surfynol 61 and white spirit were less damaging and ethanol least damaging although it scratched surfaces when applied using cotton bud and cotton cloth. Spectacles and microfibre cloths were the least damaging cleaning materials. Akapad sponge always left residues and sometimes tidelines. Cleaning with supercritical carbon dioxide induced stress cracking and opacity to HIPS. Its gloss was reduced by almost one third by this cleaning agent.

Ethanol and isopropanol were very effective at removing both sebum and organic oil soils (Figure 8). Ethanol was slightly more effective in cleaning sebum soiled samples whereas isopropanol was slightly more effective at removing organic oil soil. All cleaning materials were good at removing soils, although cotton bud, cotton cloth and leather chamois were less effective than the others.

Solvent cleaning of PMMA

Adding ethanol, isopropanol and white spirit to cleaning materials reduced scratching by a factor of ten, suggesting that these solvents also functioned as lubricants. By contrast, acetone, Surfynol 61 and xylene increased the percentage area scratched. Compared with aqueous cleaning agents, solvents were more damaging for PMMA despite the fact that double the number of rubs was used to apply the former.

Acetone damaged PMMA more than other solvents evaluated (Figure 9). Its abilities to dissolve dirt and lubricate plastic surfaces were poor and resulted in a high percentage area scratched, similar to that observed with mechanical cleaning. Ethanol was the solvent causing least damage to PMMA unless it was applied with yellow Akapad sponge. Microfibre cloth, spectacles cloth and cotton bud were least damaging materials to apply solvents.

Though all solvents caused a reversible swelling of yellow Akapad and poly(vinyl acetate) sponges, Surfynol 61 was unique in dissolving poly(vinyl acetate) sponge, which left a milky residue on PMMA surfaces after cleaning. Leather chamois also left a milky layer on surfaces when used in combination with solvents. Acetone reduced the original glass clear appearance of PMMA. Ethanol, isopropanol and xylene changed the appearance of PMMA when applied by sable hair brush, synthetic feather duster and yellow Akapad sponge. Cleaning with supercritical carbon dioxide caused severe mechanical damage to PMMA and stress cracking. No visual differences were recorded before and after solvent cleaning of PMMA. Residues deposited by cleaning materials did not change visibly on ageing.

Solvents were notably more effective than aqueous agents at removing sebum soil (Figure 10). Xylene was the most effective, followed closely by ethanol and isopropanol. Solvents also performed slightly better than aqueous agents when cleaning organic oil soil from PMMA. Ethanol was most effective with isopropanol and xylene as close runners up. For both soil types, white spirit was the least effective at removing.

Solvent cleaning of PVC

Solvent cleaning vectors were of a similar magnitude to those from aqueous treatments and varied little between solvents (Figure 11). Isopropanol produced the lowest cleaning vector and acetone the highest. When comparing results of solvent cleaning with those of mechanical cleaning, it is clear that all solvents acted as lubricants with the exception of acetone. Scratching of surfaces was reduced by a factor of five to less than one percent of cleaned areas compared with cleaning materials applied dry.

Surfynol 61 left visible residues on surfaces on evaporation. Poly(vinyl acetate) sponge was dissolved by Surfynol 61 and left a residue. Poly(vinyl acetate) sponge, sable hair brush and yellow Akapad sponge were the poorest cleaning materials. These materials, together with synthetic feather duster left residues at surfaces. No visual differences were recorded between new and solvent cleaned PVC before and after light ageing. PVC film was deformed and stiffened after cleaning with supercritical carbon dioxide, probably because plasticiser had been extracted by the process.

As described for aqueous cleaning, the method of soil application had to be adapted for PVC. Soils migrated into PVC within weeks of application. This observation emphasises the importance of cleaning soiled PVC objects soon after dirt appears. Solvents were more effective than aqueous agents at removing sebum soil from PVC (Figure 12). Isopropanol was the most effective, followed closely by ethanol and dirt was no longer visible after cleaning. Xylene was least effective at removing sebum soil. Solvents also performed better than aqueous agents at removing organic oil soil from PVC. Ethanol and isopropanol were the only solvents which removed soil so that it was no longer visible. For both soil types microfibre cloth was more effective than the other materials tested, likely due to its superior capacity.

4.2.4. Cleaning by chemical reaction

In addition to removal of soils distributed evenly over surfaces, cleaning is also used to remove stains and spots. Collectors are particularly interested in removing stains because they reduce both commercial value and interpretation of artworks. Although chemical cleaning treatments are not recommended conservation practices for plastics, two of the most well known were selected for evaluation in the project because they are used by collectors. Hydrogen peroxide is a prime ingredient in RetrObright a homemade product mainly used by collectors to remove yellowing from acrylonitrile butadiene styrene (ABS) computer casings and keyboards (http://retrobright.wikispaces.com/Using+RetroBright). Model plastics CA, HDPE, HIPS, PMMA, PVC and XPS were selected for treatment and were examined visually and for change in contact angle.

Hydrogen peroxide (30%) and citric acid (10%)

A drop of either hydrogen peroxide or citric acid was applied to surfaces by disposable syringe and samples were left for 30 minutes in a fume cupboard. As the first round of testing did not show any clear sign of damage, another drop was applied on surfaces and left for 72 hours. Surfaces were rinsed with distilled water.

Treatment with hydrogen peroxide induced visible cracks on PMMA and CA. There were no visible changes to HDPE, HIPS, PMMA, PVC and XPS after citric acid had been applied for 72 hours, but contact angle measurements indicated that surfaces had been etched. CA was severely damaged by citric acid and acquired a matt, opaque appearance. It is clear that hydrogen peroxide and citric acid require the use of health and safety equipment so are inconvenient to use for large objects. Of more importance with respect to research, both changed the surfaces of plastics irreversibly and therefore cannot be recommended as conservation treatments.

4.2.5. Conclusions of cleaning model plastics

Research into conservation cleaning of plastics is an area which had not been extensively researched prior to this project. As a result and because the purpose of the project was to investigate the subject thoroughly, it has only been possible to investigate the cleaning materials and agents which appeared most promising from literature and other sources and to limit the plastics investigated to those which appeared most in need of cleaning from condition surveys at the partners' institutes. The plastics investigated were commercially available, uncoloured and transparent CA, HDPE, HIPS, PMMA, PVC and XPS. The framework and limits of the research were evaluated by applying them to either real museum objects or study pieces as described in section 4.2.6.

Mechanical cleaning has long been perceived as the least damaging technique to remove soiling from plastics. The results obtained from project's research suggest that the risks of introducing scratches or residues by mechanical cleaning are measurable. Some plastics were clearly more sensitive to mechanical damage than others. From the model plastics evaluated, HIPS was the most sensitive followed by HDPE, PVC, PMMA and CA. Scratches could not be measured on XPS due to its inhomogeneous surfaces. Plasticised PVC scratched easily, but appeared to repair itself because plasticiser migrated to surfaces and filled scratches.

Photo micrographs revealed that although all 22 cleaning materials evaluated scratched test plastics, some scratches were shallow and therefore invisible to the naked eye. Duzzit and Scotch Brite sponges as well as all paper based products caused more scratching of surfaces than brushes and cloths. Some cleaning materials, notably Akapad yellow and white sponges, compressed air, latex and synthetic rubber sponges and goat hair brushes left residues on surfaces. These residues were only visible on glass-clear, transparent test plastics such as PMMA. HDPE and HIPS surfaces both had matte and roughened appearances after cleaning with dry-ice. XPS was completely destroyed by the treatment. No visible changes were present on PMMA and PVC.

Of the cleaning methods evaluated, only canned air, natural and synthetic feather dusters left surfaces unchanged. Natural and synthetic feather duster-, microfibre-, spectacles- and cotton-cloths, cotton bud, sable hair brush and leather chamois showed good results when applied to clean model plastics.

Most mechanical cleaning materials induced static electricity after cleaning, causing immediate attraction of dust. It was also noticed that generally when adding an aqueous cleaning agent to a cleaning material, the area scratched was reduced. This implied that cleaning agents also functioned as lubricants. A similar effect was exhibited by white spirit and isopropanol.

Based on cleaning vectors, Judith Hofenk de Graaff detergent, distilled water and Dehypon LS45 were the least damaging cleaning agents for all model plastics evaluated. None of the aqueous cleaning agents caused visible changes when used in combination with the least damaging cleaning materials. Sable hair brush, synthetic feather duster and yellow Akapad sponge were unsuitable for applying aqueous cleaning agents. Poly(vinyl acetate) sponge swelled in contact with solvents and was only suitable for aqueous cleaning processes.

Based on cleaning vectors, white spirit was the least damaging solvent. Acetone and Surfynol 61 were the most damaging for all model plastics and cannot be recommended for cleaning plastics. Surfynol 61 dissolved poly(vinyl acetate) sponge and left a milky residue on surfaces, which was particularly apparent on clear PMMA surfaces. Surfynol 61 left residues on surfaces on evaporating and acetone evaporated too rapidly to lubricate cleaning materials thereby increasing scratching of surfaces.

Supercritical carbon dioxide induced discolouration and mechanical damage to the model plastics, particularly to XPS, CA and PMMA and should not be used for conservation cleaning of plastics.

The many cleaning vectors obtained for model plastics, each of which comprises quantitative changes in gloss, contact angle and percentage of area scratched by cleaning for a particular plastic, were combined with qualitative visual assessments and after cleaning and summarised as a set of flow charts for cleaning CA, HDPE, HIPS, PMMA and PVC. The decision based flow charts are presented in Figures 13 to 17. They are intended to assist conservators optimize the removal of soil while minimising the risk of damaging the plastic types researched in the project. Flow charts are based on the results obtained and limited by the project's scope.

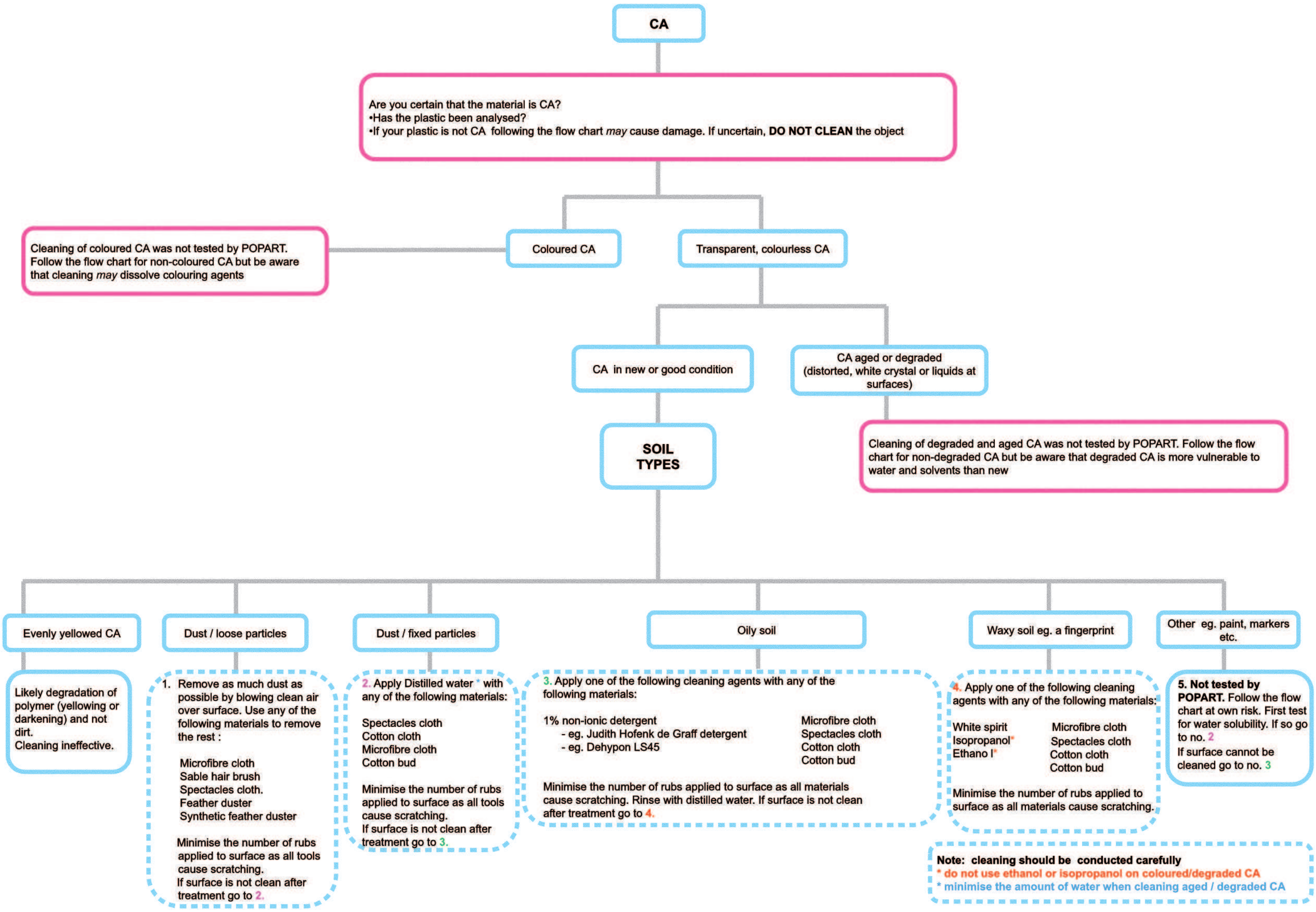

Figure 13. Flow chart for cleaning cellulose acetate (CA)

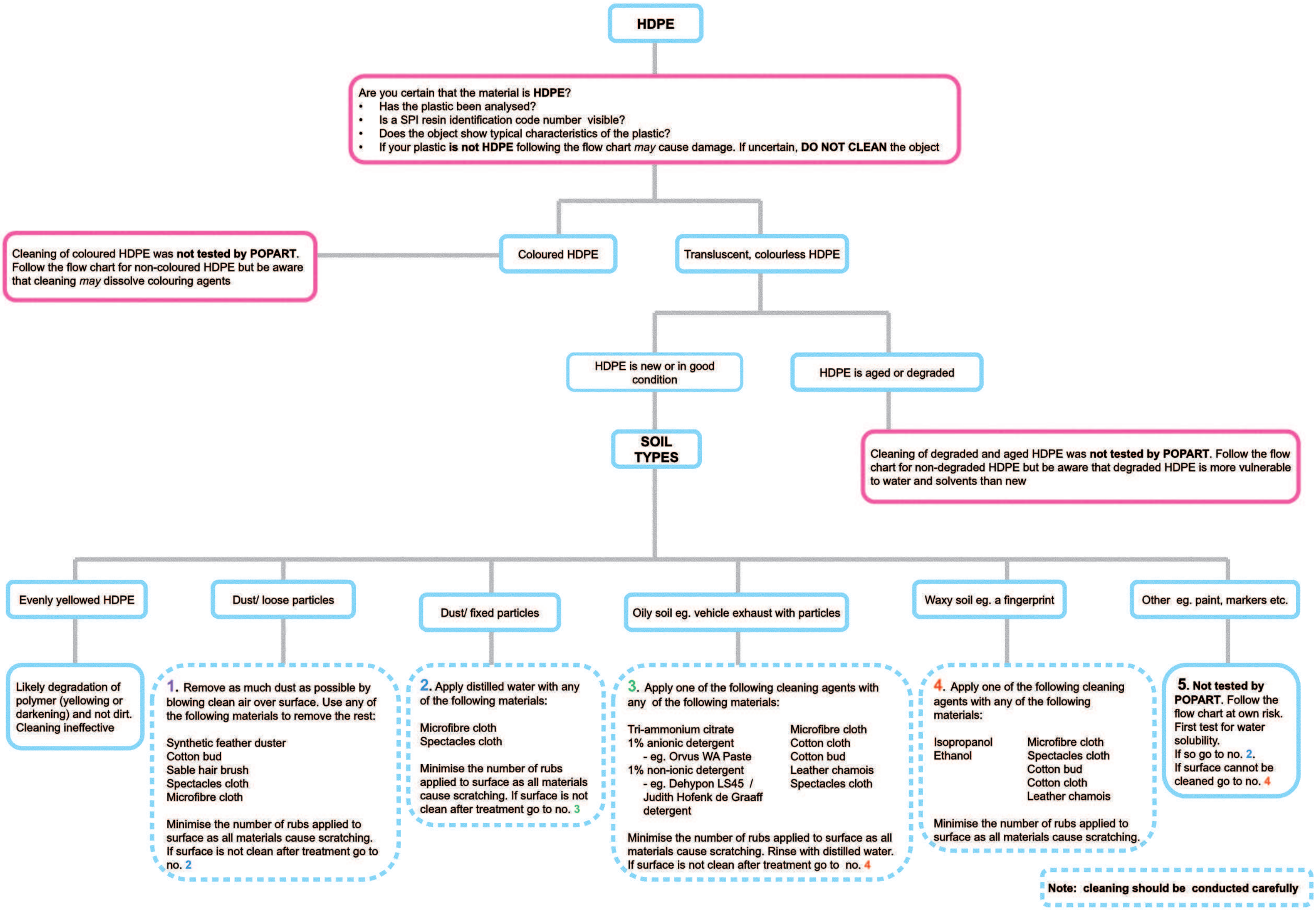

Figure 14. Flow chart for cleaning high density polyethylene (HDPE)

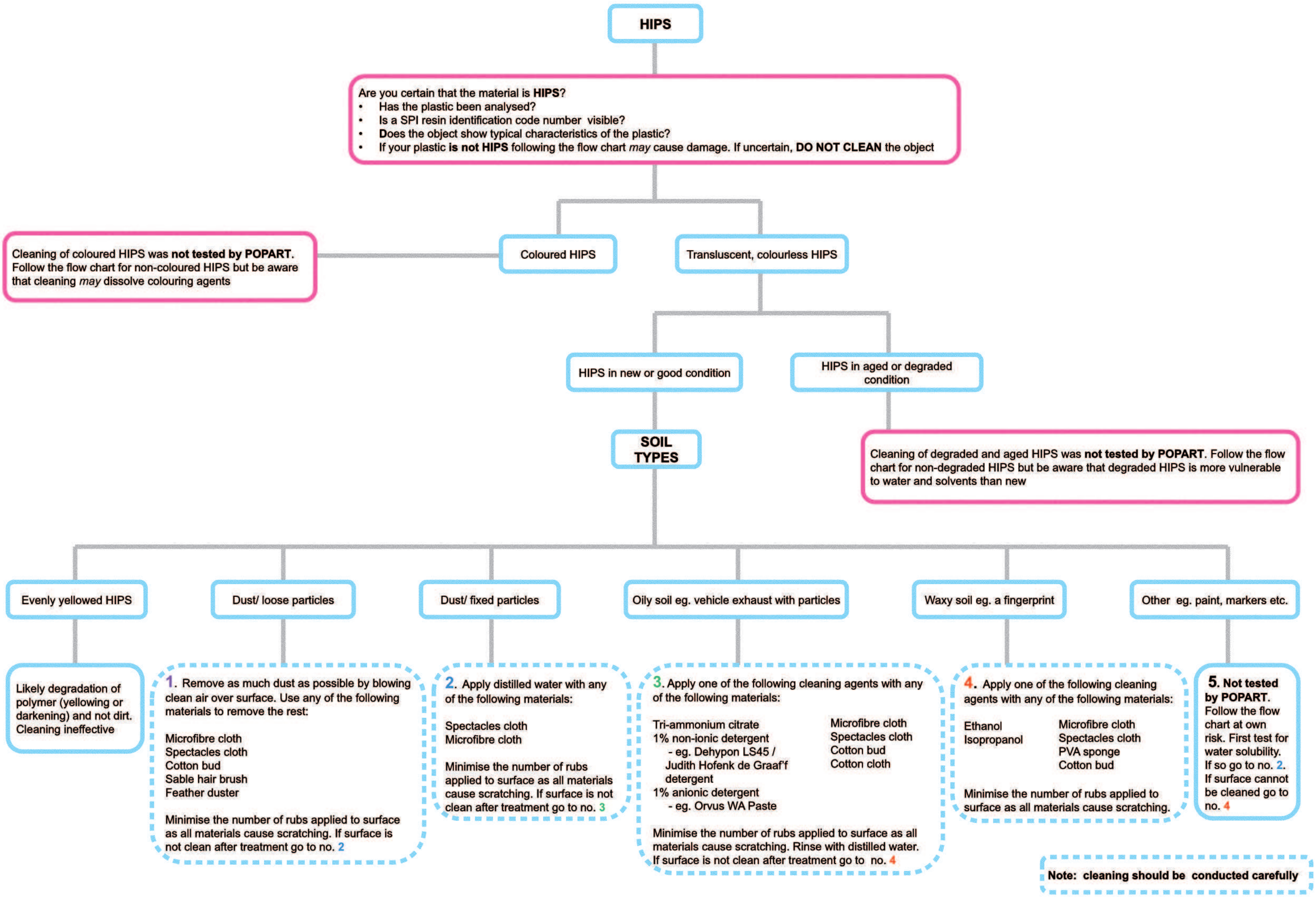

Figure 15. Flow chart for cleaning high impact polystyrene (HIPS)

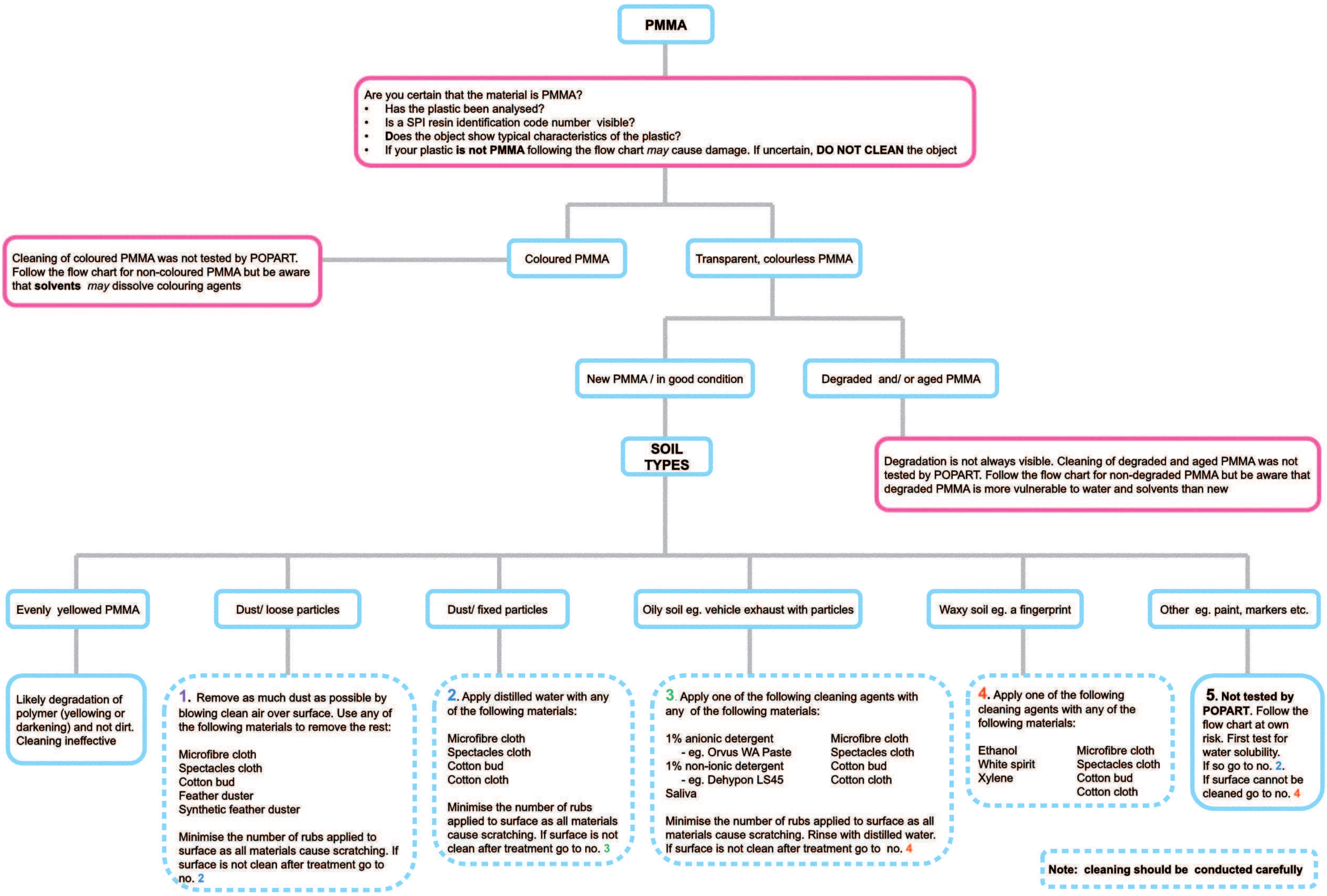

Figure 16. Flow chart for cleaning poly(methyl methacrylate) (PMMA)

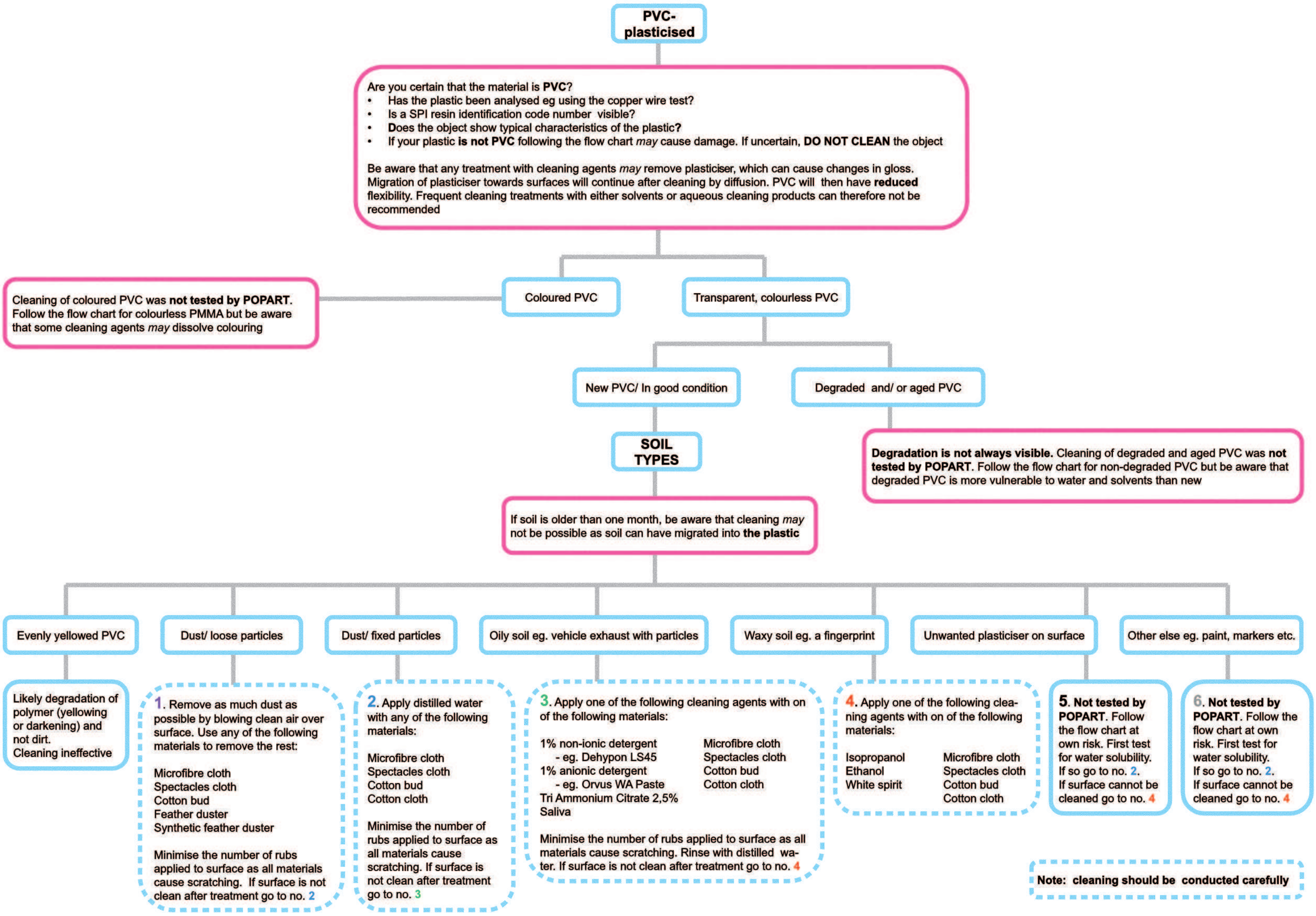

Figure 17. Flow chart for cleaning plasticised poly(vinyl chloride) (PVC)

4.2.6. Application of experimental findings to case histories

In order to test the usefulness of the many experimental results obtained during cleaning research on model plastics in the project, they were applied to actual dirty plastics selected by each partner.

Cleaning cellulose acetate (CA) – a case study

An artist's book entitled *Ombres Transparentes* (transparent shadows) of the Portuguese artist Lourdes Castro was selected as CA case study (Figure 18a). This artist's book belongs to a series of thirty similar pieces made by the artist in her studio in Paris in 1967. Each book measures 30 cm x 28.5 cm x 2 cm and contains twenty five CA sheets. In an interview with the artist, she recalled using Rhodoïd, a French trademark of CA. Fundação de Serralves Museu de Arte Contemporânea in Porto has two of those artist's books in their collection of which one was selected for cleaning.

Some of the sheets were transparent and others coloured with both matte and glossy finishes. The designs were made by silkscreen, and the cuttings were made manually using a pyrographic method. All the sheets, front and back cover were assembled with a metal spiral.

CA is dimensionally unstable due to changes in ambient temperature and humidity. Water absorption leads to dimensional changes, which cause warping, whereas water loss leads to shrinkage. Symptoms of CA degradation include distortion or warping, weeping, shrinkage, odour and blooming. The so called "vinegar syndrome" in which ethanoic acid (acetic acid) is given off by degradation of CA is the result of hydrolysis.

The book had warped sheets and some were heavily distorted. The dimensional changes were attributed to both water absorption and the type and amount of plasticiser. Some sheets have white solid material at surfaces, others have whitish stains and yet others coloured liquid deposits. Some of the liquid deposits were transferred to other sheets leaving a colour on the surface. Before cleaning the sheets, the book was dismantled by removing the metal spiral. Three sheets of the book, front cover sheet, sheets nine and ten, were selected for cleaning because of superficial dirt comprising loose and fixed particles, fingerprints, brown residues due to metal corrosion and white solid deposits.

The front cover sheet is glossy on one side, while the other side has a matt (rough) finish. Glossy and matt appearances

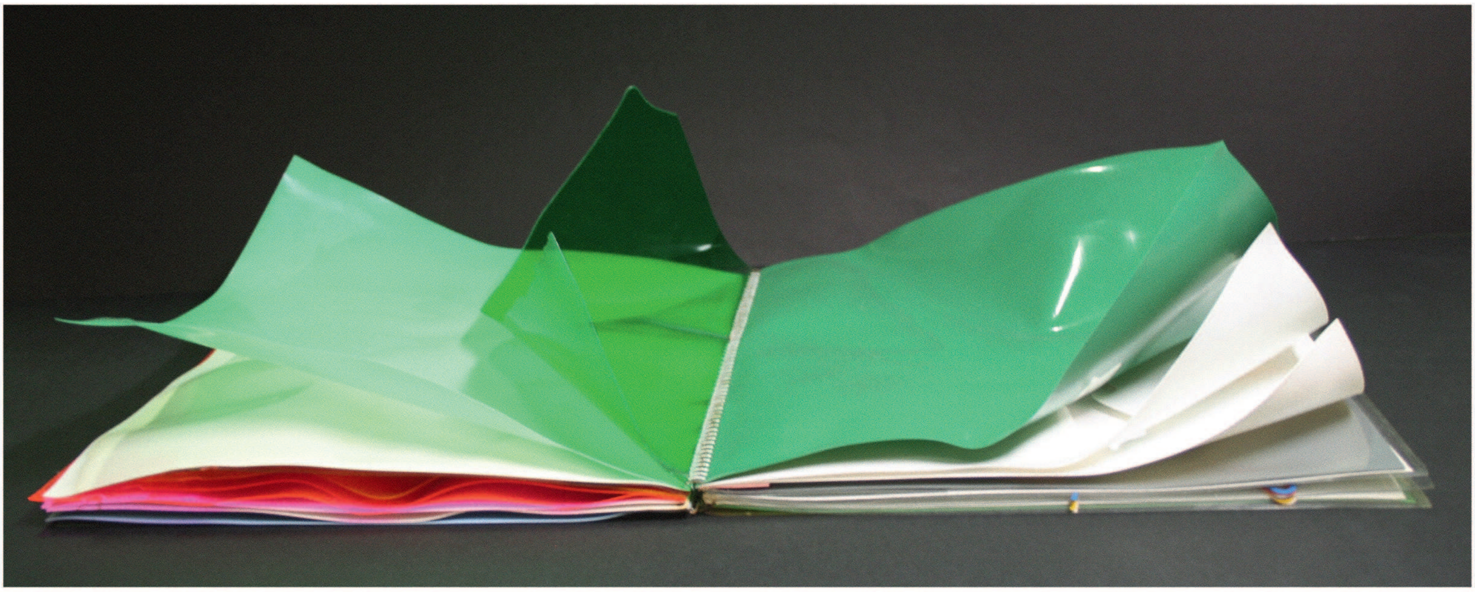

Figure 18a. Lourdes Castro, Ombres Transparentes, 1967, cellulose acetate sheets which are degraded and soiled, 30 x 28.5 x 2 cm (© Fundação de Serralves, Museu de Arte Contemporânea, Porto, Portugal, photo Ana Veiga)

had been produced during manufacture. The texts "OMBRES TRANSPARENTES" and "LOURDES CASTRO" and "ED.KWY" are printed on the cover sheet. Superficial dirt, which comprised loose and fixed particles and brown coloured residues derived from the oxidation of the metal spiral, were observed. Mechanical damage in the form of a tear could be observed alongside the punched holes in which the metal spiral was placed.

Sheet nine was a grey sheet with one glossy side which was painted with black alkyd resin paint in such a way that the grey CA sheet depicted a smoker. The reverse side of sheet nine was grey with no finish. Sheet nine was selected because it showed white solid deposits only on unpainted areas. The white solid deposits were identified as a mixture of plasticisers (di-ethyl phthalate, tri(2-cloro ethyl)phosphate and tri-phenylphosphate) using FTIR and Pyrolysis Gas Chromatography Mass spectrometry (Py-GCMS).

Sheet ten was a transparent sheet and illustrated with a cup on a plate painted with white alkyd resin paint. This sheet was selected for cleaning because it showed fingerprints and superficial dirt.

Because cleaning experiments had been performed on new pristine CA sheets, some additional trials were needed to evaluate the behaviour of the cleaning agents and cleaning materials on coloured, aged and degraded CA. Fortunately spare sheets of the same age and same composition had been donated by the artist. Cleaning tests were performed on those spare sheets.

They were cleaned with those cleaning materials and agents which had performed best in POPART experiments on model CA, namely microfibre cloth, Judith Hofenk de Graaff detergent, Dehypon LS45, distilled water, isopropanol, white spirit and ethanol.

Ethanol dissolved the solid plasticiser on the surface of the spare sheets causing a white blurry surface which was not observed when cleaning new. New CA sheets contain di-ethyl phthalate as plasticiser. Furthermore applying ethanol to aged CA sheets caused the removal of colourants that were dissolved in the plasticiser. Ethanol is therefore an unsuitable cleaning agent for aged CA. Isopropanol also caused a blurry surface. White spirit caused no visible changes to CA sheets.

In conclusion, CA spare sheets with superficial dirt, white solid deposit and fingerprints could be effectively and safely cleaned with distilled water or with detergents. It is important to minimise the amount of water when cleaning aged, degraded CA sheets, to avoid warping.

For the three sheets of the artist's book, cleaning materials were selected based on the surface structure and surface damage of the sheets. The least damaging material for mechanical cleaning CA sheets according to research on model CA was microfibre cloth. Due to its structure it was unsuitable for rough surfaces and for cleaning punched holes. Therefore, microfibre cloth was used to clean glossy sides of sheets and spectacles cloth for rough sides. These two cleaning materials were also used in combination with cleaning agents. For cleaning the tiny punched holes, a cotton bud in combination with cleaning agents was chosen. Considering the results obtained on the spare sheets, aqueous cleaning was preferred to solvents.

Most of the superficial dirt from the front cover sheet was removed using dry spectacles cloth. Remaining dirt was removed using spectacles cloth moistened with distilled water and a moist cotton bud around and inside the tiny holes. After this treatment only brown residues due to metal corrosion of the spiral remained. Based on cleaning vectors for aqueous cleaning agents, Judith Hofenk de Graaff detergent and Dehyphon LS45 were tested to remove the brown corrosion. Judith Hofenk de Graaff detergent applied with a cotton bud proved to be the most effective combination. All brown residues were removed except for one spot. Microscopic examination revealed that this spot had migrated into the cellulose acetate.

As sheet nine was glossy on one side and had no finishing treatment on the reverse side, the first treatment was to remove the loose superficial dirt with microfibre cloth taking care not to clean the punched holes. The second step was to remove the fixed particles and using microfibre cloth moistened with distilled water again taking care not to touch the punched holes. Microfibre cloth

Figure 18b. Lourdes Castro, Ombres Transparentes-detailed photograph of sheet 9 before cleaning showing white, solid deposits on the grey CA area (left) and after cleaning (right) (© Anna Laganà)

was efficient at removing all fixed particles and also the white solid deposits (plasticisers). The punched holes were cleaned with a moist cotton bud. Spectacles cloth was used to dry surfaces (Figure 18b).

Surfaces of the two sides of sheet ten were mechanically cleaned with dry microfibre cloth to remove loose particles. Then microfibre cloth moistened with distilled water was used to remove remaining superficial dirt. As for sheet nine the CA surface was dried with spectacles cloth to remove remaining moisture. Also in this case, the punched holes were separately cleaned with a moist cotton bud. No further treatment was needed because the moist microfibre cloth was also effective at removing fingerprints.

Cleaning high density polyethylene (HDPE) – case studies

The objects selected were a used Tupperware pitcher and a strainer, purchased from a flea market. The material was identified as

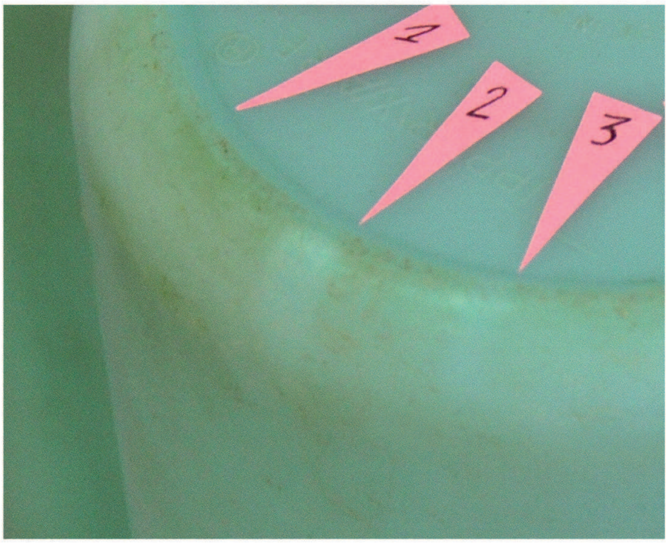

Figure 19. Detailed photograph of polyethylene pitcher showing cleaning techniques. From left to right: 1.Cotton bud/ Dehypon LS45, 2.Cotton bud/ tri-ammonium citrate, 3.Cotton bud/ isopropanol (© Clémentine Bollard)

polyethylene by FTIR spectroscopy. According to literature the objects are more likely to be made of low density polyethylene than high density polyethylene used as a model plastic in cleaning trials. However, it was thought that the chemical and mechanical properties of low density polyethylene were sufficiently close to those of HDPE to justify applying the results from cleaning model plastics.

Both objects were blue-green, injection moulded and showed trademarks indicating their production sites of Belgium for the pitcher and France for the strainer. Their production date is unknown but Tupperware has only been produced in Belgium since 1960 and in France since 1973. The pitcher was very dusty and covered in fixed particles. The outer surface showed a dark brown substance, which peeled off readily. The inner surface was stained with orange and its surface was randomly scratched, likely due to use. The strainer was dusty and covered in fixed particles. The inner surface bore an even brown coloured layer. The holes and least accessible areas showed a layer of dark brown peeling substance. The overall surface bore circular scratches consistent with use.

The type of soiling was unknown and therefore not considered a criterion by which to select cleaning techniques. Instead, selection comprised three steps. Firstly, all techniques that caused visible damages to HDPE (e.g. scratches, blurred surface, and dissolution) were discounted. Secondly, cleaning vectors for each cleaning material/cleaning agent were examined and those less than ten units were considered. The third step involved evaluating the techniques' effectiveness at removing soils. Tests on small areas were conducted on the two objects in order to find which cleaning technique would be most useful with respect to their shapes and types of dirt.

The pitcher was brushed to remove loose particles with a soft sable hair brush and the particles removed by vacuum cleaner. The brown substance was carefully removed with a scalpel blade. Cleaning techniques chosen from the list of non-damaging techniques for HDPE were tested on the fixed particles in order to determine the most effective. A detergent, tri-ammonium citrate and a solvent were applied first with cotton bud in hidden areas (Figure 19):

- 1.Cotton bud/Dehypon LS45 were partially effective
- 2.Cotton bud/tri-ammonium citrate were effective
- 3.Cotton bud /isopropanol were partially effective

Tri-ammonium citrate was effective at removing fixed particles and therefore was applied by microfibre cloth. This cleaning technique was used to clean the outer surfaces of the pitcher. In some areas (e.g. corners, scratches) the dirt was more difficult to

Figure 20. Tupperware polyethylene strainer, upper side after cleaning and lower part showing test areas: 1. Cotton cloth/ tri-ammonium citrate, 2. Microfibre cloth/ Orvus WA Paste, 3. Microfibre cloth/ Judith Hofenk de Graaff detergent, 4. Microfibre cloth/ distilled water, 5. Cotton cloth/ Dehypon LS45, 6. Cotton bud/ isopropanol, 7. Cotton bud/ ethanol (© Clémentine Bollard)

remove and stronger mechanical action required, so tri-ammonium citrate was applied with cotton bud. The local orange stains proved highly resistant. White spirit on a cotton bud was tested on the stain, without success. The orange substance had migrated into the material causing irreversible damage.

Loose particles of dust and flaking material were removed mechanically from the strainer with a sable hair brush and vacuum cleaner. Because a cotton bud was considered as the most convenient material to clean the narrow holes, it was combined with several agents of which Judith Hofenk de Graaff detergent proved the most effective. Flat areas were tested with the following combinations as shown in Figure 20:

- 1. Cotton cloth/tri-ammonium citrate
- 2. Microfibre cloth/Orvus WA Paste
- 3. Microfibre cloth/Judith Hofenk de Graaff detergent

- 4. Microfibre cloth/distilled water
- 5. Cotton cloth/Dehypon LS45
- 6. Cotton bud/isopropanol
- 7. Cotton bud/ethanol

Dehypon LS45 and Orvus WA Paste were the least efficient while Judith Hofenk de Graaff detergent, tri-ammonium citrate and distilled water all removed equal amounts of dirt. Ethanol and isopropanol also dissolved part of the dirt but left halo forms around test areas. Cotton cloth with tri-ammonium citrate was preferred as fewer rubs where necessary to obtain maximum cleaning. Nonetheless, dirt remained inside scratches afterwards, leaving an even brownish colouration.

Relating the experience of cleaning real rather than model plastics, suggested that tri-ammonium citrate, which was only partially effective at removing standard soils was highly effective at removing real soil from the pitcher. Dehypon LS45, which was highly effective at removing standard soils, was also effective at cleaning the object. Cleaning the strainer revealed that although very efficient on artificial soils, Dehypon LS45 was ineffective for the type of soil present on the object, whereas tri-ammonium citrate applied with a cotton cloth was highly effective as shown by the research on model HDPE.

Cleaning high impact polystyrene (HIPS) – a case study

A wall storage unit purchased at a flea market was selected for cleaning (Figure 21). A sticker on the back identified the designer as Jean-François Lecointe. The material was identified as polystyrene by FTIR spectroscopy and the results of cleaning model HIPS were used to test whether the cleaning practices recommended for HIPS were applicable to other types of polystyrene.

The object was bright orange and comprised two elements each of which was probably injection moulded separately and adhered together afterwards. Because the designer graduated in 1964 from the Ecole nationale supérieure des arts appliqués et des métiers d'art–Olivier de Serres, it is likely that he designed the piece after this date. The wall storage furniture was extremely dusty and covered in fixed particles. The external surface showed black marks. Both outer and inner surfaces showed marks from burning. Surfaces were randomly scratched, likely through use.

The type of soiling was unknown and therefore not a factor in selecting cleaning techniques. Selection was based on three steps. First, all techniques that induced visible damage to HIPS including scratching and dissolution were discounted. Techniques

Figure 21. Detailed photograph of wall storage furniture by Jean-François Lecointe showing cleaning: 1. Microfibre cloth/ Orvus WA Paste, 2. Microfibre cloth/ Dehypon LS45, 3. Cotton bud/ Dehypon LS45, 4. Spectacles cloth/ tri-ammonium citrate, 4'. Cotton bud/ tri-ammonium citrate, 5. Cotton bud/ ethanol, 6. Cotton bud/ isopropanol, 7. Spectacles cloth/ ethanol, 8. Large area cleaned with cotton bud/ethanol (© Clémentine Bollard)

with cleaning vectors lower than ten units were selected. Cleaning model HIPS suggested that solvent damaged much more than aqueous cleaning techniques. Comparing cleaning vectors, the most damaging solvent vector was a factor of eight higher than that for the most damaging aqueous cleaning agent. Finally, the effectiveness of cleaning treatments to remove soils was considered. Selected cleaning techniques were applied to the object to evaluate their effectiveness in reality.

Loose particles were removed using a soft sable hair brush and vacuum cleaner. Some cleaning methods chosen from the list of safe techniques for HIPS were applied:

- 1. Microfibre cloth/Orvus WA Paste were partially effective
- 2. Microfibre cloth/Dehypon LS45 were more effective than technique 1
- 3. Cotton bud/Dehypon LS45 were more effective than technique 2
- 4. Spectacles cloth/ tri-ammonium citrate were less effective than technique 2
- 4'.Cotton bud/tri-ammonium citrate were more effective than technique 4

None of the aqueous techniques resulted in a satisfactory level of cleaning.

Although according to experimental results on samples, solvent based cleaning techniques were more damaging than aqueous, it was decided to evaluate the two least damaging solvents, namely ethanol and isopropanol.

- 5. Cotton bud/ethanol were very effective
- 6. Cotton bud/isopropanol were very effective

Both techniques proved to be very effective and gave very satisfactory results. Even though no visible scratches were noticed, it was decided to perform a last test with spectacles cloth combined with ethanol which is the least damaging solvent based on cleaning vectors.

- 7. Spectacles cloth/ethanol were less effective than technique 5

This softer technique was less satisfactory and it was decided to clean using ethanol with a cotton bud. To lower the potential of cotton buds to scratch, a large cotton wool ball was used instead. To avoid the development of white halos due to fast evaporation of ethanol, the surface was rinsed immediately with demineralised water and dried with a spectacles cloth. In addition to removing the general black soil, this treatment, repeated several times, was also effective at removing the black marks.

Cleaning polymethylmethacrylate (PMMA) – a case study

Light Sculpture without Light, made in 1976 by Danish artist Gunnar Aagaard Andersen (1919-1982), belongs to the Danish National Gallery. The sculpture comprises of several white, acrylic sheets which have been glued together like a series of open boxes inside each other, almost as a minimalist version of a babushka doll. Structurally some joins have failed, which means that the sculpture cannot be viewed standing as originally intended. The sculpture was covered with an even layer of dark soil, identified as oily dirt containing particles. In addition the lower part of the sculpture was severely scratched. Most scratches were filled with soil which darkened the object's appearance.

Cleaning research into model PMMA had shown that solvents had performed slightly better than aqueous cleaning agents when cleaning off organic oil soil, but because the artwork was more than 30 years old and degraded, caution was required. A selection of aqueous cleaning agents was tested along the lower edge of the sculpture.

Orvus WA Paste performed best, followed by tri-ammonium citrate and Dehypon LS45. The findings corresponded with the results of the research on model PMMA. As Orvus WA Paste had proved least damaging it was selected to clean the lower sections. Orvus WA Paste was applied with microfibre cloth, which was the material which caused least mechanical damage.

The even layer of soil was successfully removed with Orvus WA Paste. However, black soil which had accumulated in recessed areas could not be removed using microfibre cloth. Instead, most soil could be removed with Orvus WA Paste applied with a cotton bud. For cleaning to be successful rubs had to be applied in the same direction as the scratches. After cleaning, surfaces were rinsed with distilled water. Not all black soiling could be dissolved by aqueous cleaning agent, so the effect of solvents was carefully tested and ethanol applied by cotton bud found to remove the last traces (Figure 22).

The practical cleaning of *Light Sculpture without Light* showed that the results of the POPART project could successfully be transferred to a real object. However, the practical cleaning also raised a question for further research. Whilst cleaning it was noticed that it was easier to clean an area if the cleaning agent was allowed

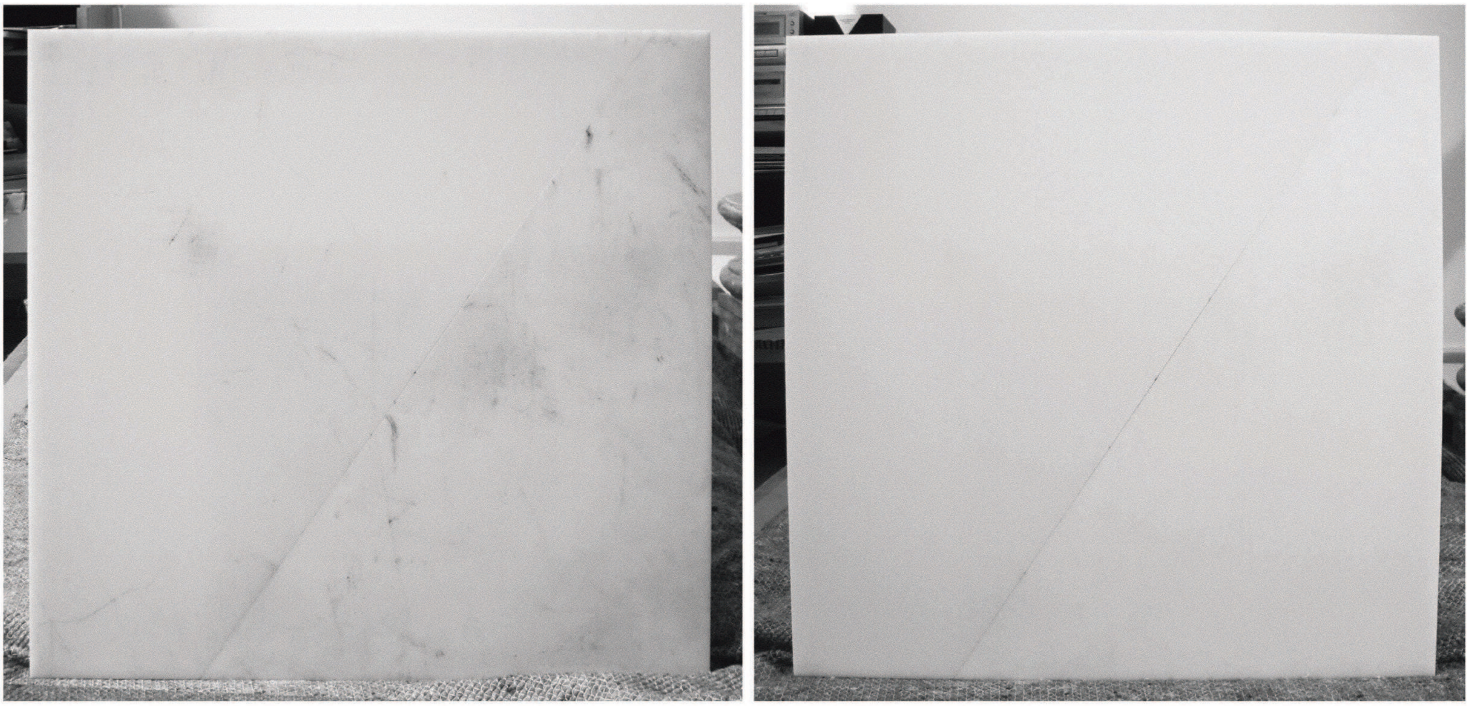

Figure 22. Detailed photograph showing base of Gunnar Aagaard Andersens' Light Sculpture without Light from 1976, before (left) and after (right) cleaning (© Kathrine Segel)

to "sit" for a while. This observation suggested the use of gels, poultices and other methods to soften soil layers, which was not studied. The practical cleaning also emphasized that even though cleaning materials such as microfibre cloth clearly emerged as less damaging to flat, pristine plastic surfaces, real three dimensional museum objects with uneven shapes and damaged surfaces, can only be successfully cleaned using other cleaning materials.

Cleaning plasticised poly(vinyl chloride) (PVC) – a case study

In order to examine how cleaning research on model, new PVC related to real museum objects, one of the crash test dummies belonging to the Science Museum in London was selected as a test object. The dummy was made in the mid 1970's and acquired by the museum in 1979. Crash test dummies were used to model the motion of a human driver when applying the brakes of a vehicle and to predict any injuries arising from not wearing a seat belt. The dummy comprised a mechanical, steel structure to replicate the weight and movement of a human being and was covered with plasticised PVC skin to add textural and cosmetic properties.

After 10 years on display in a closed showcase, all surfaces had become shiny and sticky. After 15 years, phthalate plasticiser started dripping from the PVC covering the object's head, hips and feet. Dust adhered to the sticky surfaces. FTIR spectroscopy revealed that the dummy was made of red PVC, around 15 mm thick which was attached to the internal steel frame. The red PVC has a thin flesh-coloured PVC coating which was reaily abraded. If the dummy was damaged during crash tests, red PVC was revealed under the pink surfaces.

According to FTIR spectroscopy, the object's soil layer comprised phthalate, carbon particles and unidentified red pigment. Phthalate plasticiser and carbonaceous dirt are frequently present at surfaces of PVC toys and photograph pockets in museum collections. PVC cleaning research had shown that differences in levels of induced damage and effectiveness between aqueous cleaning products and solvent such as ethanol and isopropanol were minor. As the selected test object was visibly degraded and too large to be placed easily in a fume cupboard, aqueous cleaning was the preferred approach.

Initial cleaning tests using microfibre cloth and detergents were performed by the National Museum of Denmark. Afterwards, Science Museum conservation staff, none of whom had participated in the trials, were instructed in how to perform the actual cleaning using guidelines based on research. The purpose of this approach was to evaluate how conservators would use results in reality.

Conservators found that soil and plasticiser could be removed using both Dehypon LS45 and Orvus WA Paste applied by microfibre cloth (Figure 23). It was decided to clean the dummy using the latter. Detergent was applied by cotton bud in areas that were hard to access. Cleaning was carried out under a microscope. After cleaning, PVC had neither shrunk nor embrittled. No new plasticiser to replace that removed by cleaning had migrated to surfaces in the weeks following the cleaning.

Nathalie Balcar, Gilles Barabant, Clémentine Bollard, Sara Kuperholc, Brenda Keneghan, Anna Laganà, Thea van Oosten, Kathrine Segel and Yvonne Shashoua

Figure 23. Crash Test Dummy child during removal of plasticiser and soil from its right leg with Orvus WA Paste and microfibre cloth/cotton bud (© Science Museum, London, photo by Jennie Hills)