Survey of chemical substances in consumer products

Survey no. 16 - 2002

Cleaning materials and polishes for metal

Cand. Pharm. Jette Laursen Chemtox A/S

Contents

| SUMMARY AND CONCLUSIONS 1 INTRODUCTION 1.1 CLEANING MATERIALS AND POLISHES AS CONSUMER PRODUCTS 1.2 PRODUCT TYPES 1.3 EXTENT OF THE PROJECT 10 |
|--|
| 1.1CLEANING MATERIALS AND POLISHES AS CONSUMER PRODUCTS81.2PRODUCT TYPES81.3EXTENT OF THE PROJECT10 |
| 1.2 PRODUCT TYPES81.3 EXTENT OF THE PROJECT10 |
| |
| |
| 2 AVAILABLE CLEANING MATERIALS AND POLISHES 11 |
| 2.1 RETAIL TRADE 11 2.2 INTERNET 11 |
| 2.3 PRODUCT SURVEY 12 |
| 3 SURVEY OF FINISHED PRODUCTS 13 |
| 3.1 CLEANING MATERIALS AND POLISHES FOR SILVER 13 |
| 3.1.1 Content of chemical substances in polishes for silver objects 14 |
| 3.1.2 Assessment of product information on polishes for silver 15 |
| 3.2 CLEANING MATERIALS AND POLISHES FOR GOLD 16 3.2.1 Content of chemical substances in polishes for gold and iewels 16 |
| 3.2.1 Content of chemical substances in polishes for gold and jewels 16 3.2.2 Evaluation of product information of polishes for gold and jewels 17 |
| 3.3 CLEANING MATERIALS AND POLISHES FOR COPPER/BRASS 17 |
| 3.3.1 Content of chemical substances in polishes for copper/brass 18 |
| 3.3.2 Evaluation of product information on polishes for copper/brass 18 |
| 3.4 CLEANING MATERIALS AND POLISHES FOR STEEL AND OTHER |
| METALS 19 |
| 3.4.1 Content of chemical substances in polishes for steel and other materials 19 |
| 3.4.2 Evaluation of product information on polishes for steel and other metals2 |
| 4 REVIEW OF DIY-RECIPES AND PRODUCTS 21 |
| 4.1 RECIPES OF DIY-PRODUCTS 21 |
| 4.1.1 Silver 21 |
| 4.1.2 Gold 21 |
| 4.1.3 Copper/brass 21 |
| 4.1.4 Other metals 4.2 THE FUNCTION OF CHEMICAL SUBSTANCES 22 |
| |
| 5 SURVEY OF INDIVIDUAL SUBSTANCES AND SUBSTANCE GROUPS ACCORDING TO FUNCTION 23 |
| 5.1 Surfactants 23 |
| 5.2 ABRASIVES/POLISHES 23 |
| 5.3 Brighteners/inhibitors 24 |
| 5.4 ORGANIC SOLVENTS 24 |
| 5.5 ACIDS/BASES 25 |
| 5.6 WAX 25 |
| 5.7 THICKENERS 25 |
| 5.8 PRESERVATIVES 26 |
| 5.9 WETTING AGENTS 26 5.10 PERFUME AND DYE 27 |

| | 5.11 | ACCESSORY AGENTS | 27 |
|---|------|---|----|
| 6 | C | ONCLUSION | 28 |
| | 6.1 | AVAILABILITY OF CLEANING MATERIALS AND POLISHES | 28 |
| | 6.2 | QUALITY OF INFORMATION GATHERED | 28 |
| | 6.3 | EVALUATION OF INGREDIENTS | 29 |
| | 6.4 | EFFICIENCY | 29 |
| | 6.5 | ECO-LARFLLING | 29 |

Preface

This report contains the results of the project "Cleaning materials and polishes for metal" which is a part of the Danish Environmental Protection Agency's overall effort in connection with the mapping of chemical substances in consumer products.

The project is carried out by Chemtox A/S.

To evaluate the progress and results of this project the following group has been appointed:

Claus Ankjærgaard, The Danish Environmental Protection Agency (project manager) $\,$

Jette Laursen, Chemtox A/S

Shima Dobel, The Danish Environmental Protection Agency

Summary and conclusions

The market has been searched for available cleaning materials and polishes, which ordinary consumers can buy.

This project is focused on cleaning materials and polishes for metal articles which are in contact with skin, eg. jewellery and watches or metals which are used in connection with food eg. cutlery.

The market has been examined partly by purchasing products in five convenience stores and seven specialist shops, partly by uncovering the market through the internet.

25 different products have been bought. In convenience stores you find products from some suppliers, whereas the products sold in specialist shops come from other suppliers.

All products can be used to clean or polish silver, gold, copper, brass as well as steel and other types of metals.

Searches on the Internet have confirmed that a large part of the products available for the consumers at the Danish market was found. Recipes can also be found on the basis of which people can mix the own DIY-products to clean and polish metals with only a few chemical substances.

14 of the products can be used for silver, four products can be used for gold, four products for copper and brass and three products for steel and other metals. It has not been possible to obtain supplier safety data sheets or complete formulations of all products.

The information gathered in the shape of formulations and safety data sheets of the products has been compared with the information on the packaging of all products.

Overall cleaning materials and polishes are available in three different states which influences the way they are used and therefore also the chemical composition of the products. The three types are liquids made for dipping, polish to be applied with a cloth or impregnated textiles. Cleaning with dipping liquids is purely chemical whereas the other two types use a combination of chemical and mechanical cleaning of metal surfaces. Therefore, dipping products contain more aggressive chemical substances but on the other hand there is not any skin contact with these products.

The polish products and impregnated textiles are chemically alike. The only difference in these products is that you need to have a cloth for polish-products, which is not the case by impregnated textiles. Chemical substances requiring long-term contact with the metal surface and abrasives and polishers are used, and the mechanical cleaning supplements the chemical cleaning.

The DIY-products are made of relatively few chemical substances and are based on the above mentioned types of cleaning materials and polishes.

In the project the harmful and environmentally hazardous characteristics of the substances have been examined in general. The result of this examination focuses on the use of nonylphenolethoxylates, thiourea, preservatives, dyes and perfumes in the cleaning materials and polishes. Nonylphenolethoxylate is unwanted in the outside environment whereas health effects may be discussed in connection with the other substances. Thiourea is suspected of being carcinogenic and reproduction toxic. The preservatives are suspected of being allergenic, whereas the dyes and perfumes do not have any function in the cleaning materials and polishes.

This project does not contain an evaluation of the effectiveness and durability of the cleaning materials and polishes.

1 Introduction

1.1 Cleaning materials and polishes as consumer products

The typical Danish family is every day in contact with metal objects which are made from materials requiring cleaning or polishing. Metals are oxidised by the oxygen in the air or become dirty during use and thus a maintenance of the original appearance requires a frequent cleaning or polishing.

The typical metals are gold, silver, copper, brass, bronze, zinc, steel and chromium-plated surfaces.

Metal objects can be grouped as follows:

- 1. objects which are in contact with skin
- 2. objects which are used in connection with food
- 3. objects which are used in private households
- 4. materials and objects which are mainly used outdoors in connection with maintenance, repair or hobby activities.

Group 1 comprises jewellery and watches that are constantly in contact with skin. Products, which remove the oxide layer, sebum and dirt, are used to clean jewellery and watches. These products can be purchased at goldsmiths and watchmakers, who also use similar products.

Group 2 has to do with cutlery, pots, cops, plates and other tableware which consumers use for cooking or eating/drinking. The products for cleaning and polishing will not be in direct contact with humans, but it may rub off on food and beverages.

Group 3 comprises metal objects which are used in private households but which only rarely get in contact with humans. This may be lamps, vases, door handles and musical instruments.

Group 4 has to do with the objects, which are not comprised by the other three groups including chromium-plated parts on bicycles, cars, boats and the like. The use of cleaning materials and polishes within this area is often for hobby activities, and therefore the use may be very intense in some periods during which there may be skin contact with these products, but normally there will not be any direct skin contact during use.

1.2 Product types

Ready-for-use products are available on the Danish market. Generally there are two types: a cleaning fluid in which objects can be dipped and a cleaning fluid which has to be rubbed on to the object by means of a cloth. There are also textiles, which are impregnated with cleaning materials/polishes and with which the object just has to be wiped.

However, it has also become popular to manufacture your own products to be used at home in connection with the TV-presentation of "easy" solutions to maintain miscellaneous objects.

When you use dipping-products, which are thin fluids, you can quickly clean your metal objects. You only have to dip the object shortly (in some cases less than a minute) and then rinse and wash it in water and wipe it off. This fluid easily gets into small corners. By this method the metal oxides are attacked chemically by the ingredients, and there will not be any protective film. This means that the durability of this cleaning is less than by products added with a cloth.

The durability of cleaning/polishing in which metal objects are rubbed with a polish is generally longer but the process is also longer. These products are added with a cloth and then the objects have to be polished with a clean cloth. In connection with the use of very compact polishes the object has to be wet before polishing and rinsed with water afterwards. If the object has to be used in connection with food and beverages it always has to be washed before use.

The thicker the polish the harder it will be to get into all corners during the cleaning and subsequent polishing. By this method a mechanical as well as a chemical removal of metal oxides takes place. These products contain abrasives as well as polish which makes the mechanical cleaning together with the cloth. The products also contain substances that chemically attack the metal oxides.

The longer durability of the cleaning is owing to the fact that these products leave an oil/wax layer that protects against the oxygen of the air. The durability is thus longer if the objects are not washed after polishing.

The impregnated textiles are cloths with creamy cleaning materials and polishes. Some of the textiles are shaped like gloves which makes it easier to polish especially large areas, but it may be difficult to get into all corners. The durability of this type of polishing corresponds to the use of creamy cleaning materials and polishes, as the composition and the method of these products are very similar.

No matter which type of cleaning material and polish we talk about they all contain substances which can remove the oxide layer on the surfaces of the metals chemically. These substances, which are called inhibitors, reduce the metal oxides and see to it that the surface can only difficulty be attacked by the oxygen of the air, and thus they protect the surface. The strong acids may also remove the metal oxide layer.

Abrasives and polishes are solid particles in cleaning materials and polishes, and they function by removing the metal oxides from the surface mechanically. The physical shape of the particles and the hardness is crucial for removing the oxides. If the particles are too hard, they are going to scratch the metal instead of making it gloss.

The inhibitors and the abrasives/polishes are thus the central substance groups in the cleaning materials and polishes. To support these functions ancillary materials may be added. Surface-active substances degrease the surface, thus making it easier for the chemical substances to attack the surface by reducing the surface tension.

Some organic solvents degrease but may also function as solvents to some other organic ingredients eg. wax. Finally, organic solvents may leave a glossier surface through a quick evaporation.

Polymers, wax and the like may be added in cleaning materials and polishes to give a glossy surface, and simultaneously they may form a protective film so the oxygen of the air cannot attack the metal surface.

All mentioned groups of ingredients directly or indirectly contribute to the cleaning/polishing of the metal surface.

Substances are also added to cleaning materials and polishes to be able to manufacture and use the products optimally. This may be thickeners, which are added to give the product the right consistency, which makes it possible to use it without any running. Acids and bases may be added to ensure that the product has a acidity that ensures an optimal effect of the other ingredients. Preservatives are added to aqueous products to ensure the durability of cleaning materials and polishes. Finally, dye and perfume may be added to the products to make the experience of the product more positive.

1.3 Extent of the project

The project primarily focuses on products used in private households. The project comprises ready-for-use as well as homemade products and impregnated cloths and the like.

Based on possible risks, cleaning materials and polishes used for metal objects, which may get in contact with skin, food and beverages, are given a higher priority. Therefore, products for metal objects in group 4 are not included and only a few products from group 3 are included (those products which are used in group 2 as well as group 3).

The project has been carried out in the following phases:

- Phase 1: To form a view of accessible cleaning materials and polishes in product group 1 and 2.
- Phase 2: Collecting informative labels by purchasing products.
- Phase 3: Contact to suppliers and/or manufactures
- Phase 4: Reporting based on groups of ingredients according to function. The dangerousness of substances is generally described.

2 Available cleaning materials and polishes

2.1 Retail trade

In this project importance has been attached to uncovering as large a number of products as possible on the Danish market. The availability of products in retail shops has been the criterion for the selection.

In connection with this the range was uncovered at three types of distributors:

- 1. Convenience stores/chains
- 2. Specialist shops, selling metal goods to be cleaned and polished.
- 3. Druggists.

Five different convenience stores were visited of which four each represent one of the large chains on the Danish market: Føtex, Brugsen, Aldi and Spar. The latter is an independent grocer. All shops have goods from the same suppliers but the range is a bit different.

In addition to the above three jewellers, one combined jeweller and watchmaker, one watchmaker and two ironmongers were visited. The suppliers to these stores do not overlap that much. The watchmaker did not sell cleaning materials and polishes, however he used polishing cloths at his workshop. None of the specialist shops sell the products, which can be found in the convenience stores. The specialist shops have a wide range, and generally they offer a great opportunity to get counselling in the use of the products. In many specialist shops they use the products on their own goods, eg. at the jewellers at which all products get a quick shine-up with impregnated cloths.

The same products can be found at the druggist as at the convenience stores, and pure substances as well as recipes of how to make your own cleaning materials and polishes are also available.

In this project it has been possible to purchase products for cleaning and polishing objects, which get in contact with skin or which are used in connection with food corresponding to the metal objects mentioned in group 1 and two in the introduction, in the above stores.

2.2 Internet

In addition to identifying the range at the retail market searches were also made on the Internet with the purpose of examining if the products found in the shops cover the accessible products on the market.

The internet has been used to examine the possibilities of finding cleaning materials and polishes with either reference to places at which they can be bought or with specific advises and recipes.

We have also tried to find websites at which suppliers and manufactures present their products with perhaps information in the shape of data sheets. Some suppliers and manufactures of cleaning materials and polishes were found as well as some guidelines and recipes of miscellaneous products. Supplier/manufacture names found via the Internet and those used in retail trade agreed well. The guidelines and recipes found are often described as household remedies, "green" or the like. These guidelines are base on simple recipes containing substances which are sold in most retail shops. The Internet addresses found are mentioned in appendix A.

2.3 Product survey

In retail stores products/product series were found from the following suppliers:

- Reckitt & Colmann (two products)
- Sterling (seven products)
- Henkel (one product)

These cleaning materials and polishes are for polishing silver and copper/brass. No products are only intended for gold. One product is intended to polish metals in general.

At jewellers products/product series were found from the following suppliers:

- Connoisseurs (five products)
- DELU (one product)
- Hagerty (seven products)

The products are mainly for polishing silver, gold and general jewels.

At the ironmongers products were found from the following suppliers:

- Raadvad (one product)
- Stuckmann Chemie GmbH (one product)

These two products have to be described as all-round-products, as they can be used to polish several types of metals, among others steel, copper, nickel, chromium, tin, brass, gold and aluminium.

The goods found at the ironmonger corresponded with the goods found at retail stores as well as a small leaflet with a description of how to mix your own cleaning materials and polishes on the basis of pure substances.

25 products were purchased and D.I.Y. recipes for eight different substances were found.

3 Survey of finished products

Information has been gathered about cleaning materials and polishes for different types of metal (silver, gold, copper, brass, steel and other metals). Cleaning materials and polishes for copper and brass are treated as one. Based on the type of metal, different chemicals are used to remove oxidising metal coatings. Silver is the metal which can stand the most, and the next are copper and brass. Gold cannot endure the same strong substances, so more gentle cleaning materials and polishes are used for gold. Jewels with pearls or the like are cleaned with corresponding gentle products.

In the review below products to polish jewels in general are therefore placed under cleaning materials and polishes for gold. The division is based on written information on the products as well as guidance received in the shops.

3.1 Cleaning materials and polishes for silver

Information has been gathered on 14 products, which can be used as polishes for silver. These products are available in specialist stores as well as retail stores.

Polishes for silver can be organised according to application:

all sizes of silver objects:

- creamy products, which have to be added with a cloth
- impregnated textile products in the shape of cloths and gloves in which the polish is in the fabric.

small objects, eg. jewels:

 liquid products into which objects can be dipped. The packaging is shaped for this use. Subsequently, the objects are rinsed under water and dried off with a soft cloth.

cutlerv

 liquid products into which objects can be dipped. The shape and size of the packaging is fitted for cutlery. After cleaning the cutlery is rinsed and washed.

3.1.1 Content of chemical substances in polishes for silver objects

The polishes purchased to clean silver are stated below in table 3.1 a, b and c. The tables contain information about trade name, ingredients mentioned on the packaging and in the safety data sheets from suppliers/manufactures and finally ingredients' function.

Table 3.1 a. Liquid products for silver objects

| Liquid products | | | |
|-----------------------|--------------------------|-------------------------------------|-----------------------|
| Product name | Ingredients on packaging | Ingredients according to data sheet | Ingredients' function |
| Sterling sølvrens | Thiourea | Thiourea: 1-5% | Inhibitor |
| Hagerty Silver Clean, | Thiourea: 1-7% | No data sheet | Inhibitor |
| 500 mľ | Non-ionic tensides: <5% | | Surfactant |
| | Phosphates:<5% | | pH-adjustment |
| Hagerty Silver Clean, | Thiourea: 1-7% | No data sheet | Inhibitor |
| 150 ml | Non-ionic tensides: <5% | | Surfactant |
| | Phosphates:<5% | | pH-adjustment |
| Connoisseurs Silver | Thiovrea = Thiourea | Thiourea 7% | Inhibitor |
| Jewellery Cleaner | | Sulphuric acid | pH-adkustment |

b. Creamy products for silver objects

| Creamy products | reamy products | | |
|--|--|-------------------------------------|--|
| Product name | Ingredients on packaging | Ingredients according to data sheet | Ingredients' function |
| Sterling sølv beskytter- og pudsemiddel | None | Ethanol: 5-10% 2-propanol: 5-10% | Solvent Solvent |
| Sterling Bistro Silver Cleaner | None | Ethanol: 1-5% 2-propanol: 1-5% | Solvent Solvent |
| Silvo | None | 2-propanol: 5-10% | Solvent |
| Hagerty Silver Care | Abrasive: 25% Phosphates: 1,6% Dekantiol: 3,7% Synthetic tenside: 2,1% Glycerol: 4,9% Pigments Perfume | No data sheet | Abrasive pH-adjustment Solvent Surfactant Solvent Pigments Perfume |
| Hagerty Silver polish | Polish Solvent Corrosion inhibitor Thickener Pigments Perfume | No data sheet | Abrasive Solvent Inhibitor Thickener Pigments Perfume |

c. Textile products for silver objects

| Textile products | | | |
|--|--------------------------|---|-----------------------|
| Product name | Ingredients on packaging | Ingredients according to data sheet | Ingredients' function |
| Sterling sølvpudseklud | None | Naphtha(petroleum), hydrodesulfurised heavy (< 0,1% benzene): 1-5% Risinus oil sulphated, sodium salt: 1-5% | Solvent |
| Sterling imprægneret pudsehandske | None | Naphtha(petroleum), hydrodesulfurised heavy (< 0,1% benzene): 1-5% Risinus oil sulphated, sodium salt: 1-5% | Solvent |
| Hagerty Silver duster | None | No data sheet | - |
| Hagerty Silver gloves | None | No data sheet | - |
| Connoisseurs Silver Jewellery Polishing Cloth | Cotton fibres 100 % | No dangerous substances | - |

The review of cleaning materials and polishes for silver shows that chemically they can be divided into two main groups.

- 1. products which are dipped
- 2. products for traditional polishing.

The four purchased dipping products are all based on thiourea possibly mixed with surfactants.

In connection with the actual polishes for silver the consistency of the product formulations is not the same. Three thin, creamy products, two firm cream products and five impregnated textile products were bought of which two were gloves.

The following ingredients are present in the 14 found products to polish silver:

- surfactants which can remove grease and dirt
- abrasives/polishes which ease cleaning
- inhibitors/lustring agents
- organic solvents, which quickly evaporate leaving a glossy glow
- wax or the like forming a protective film impeding the oxygen of the air getting to the surface
- polymers added to make the products more viscous
- preservatives
- perfume and dyes.

Each product comprises some of these substance types. The textile products are impregnated with products corresponding to the ones in thin products.

3.1.2 Assessment of product information on polishes for silver

Product information on the packaging has been compared with the available information in the shape of formulations and data sheets.

3.1.2.1 Products for dipping

The products for dipping all contain thiourea.

Thiourea has the following classification on the list of dangerous substances: Xn; R22, Carc3;R40 Rep;R63 N;R51/53,

which means that products with a content of more than 1 % thiourea have to be classified "Harmful" with R40' (Possible risk of irreversible effects). By concentrations larger than 5% thiourea the product also has to be classified with R63' (Possible risk of harm to the unborn child).

3.1.2.2 Creamy products

Among the five creamy products it has been possible to procure data sheets of three, and among these three it has been possible to procure formulations of two. According to the packagings of these two products they are not dangerous in accordance with the classification rules of the Danish Environmental Protection Agency, as neither danger symbols nor R- and S-phrases are stated. Of the products for which we have received formulations as well as data sheets the information in these agrees well with the information on the packaging. When ordering the safety data sheet of the supplier you are

informed that two of the products contain organic solvents. According to regulations it is not necessary to inform about this on the packaging.

3.1.2.3 Textile products

It has been possible to obtain safety data sheets on three of the five textile products as well as the formulation of the agent used to impregnate the textiles of two of the products. However, it is not stated how much agent is added to each gram textile. None of the five packagings contain information about which substances the textiles are impregnated with. For the two textile products of which formulations have been received, it is evaluated that the composition of agents for impregnation of textiles corresponds to the composition of the creamy products described in section 3.1.2.2. It is evaluated that the products of which we have received formulations and data sheets do not have to be labelled. This means that it is okay to leave out information on the packaging. However, to be able to draw a final conclusion information is missing on two products.

3.2 Cleaning materials and polishes for gold

Two products have been found which are intended particularly for gold, and two products which are used in general for jewels. One of these products can be used if a product also consists of eg. pearls, which disagree with strong detergents.

Polishes for gold can be divided into:

all sizes of golden objects:

impregnated cloths containing polish.

small objects eg. jewels:

 liquid products into which objects can be dipped, and the packaging is shaped in accordance with this.

3.2.1 Content of chemical substances in polishes for gold and jewels

The polishes purchased to clean gold are listed below in table 3.2 a and b. The tables contain information about trade name, ingredients on the packaging and in the safety data sheet of the supplier/manufacturer and finally the ingredients' function.

Table 3.2. a. Liquid products for golden objects

| Liquid products | Liquid products | | |
|----------------------------|---|---|---|
| Product name | Ingredients on packaging | Ingredients according to data sheet | Ingredients' function |
| Silbo Goldbad | Non-ionic tensides: <5% Mineral acid Sulphur compounds Alcohol | Fatty alcoholpolyglucolether Hydrochloric acid | Surfactant pH-adjustment Inhibitor Solvent |
| | Dissolution promoting substance Perfume Pigments | Propan-2-ol 2-butoxyethanol | Solvent - Perfume Pigments |
| Connoisseurs Pearl Cleaner | No pigments, harmful perfumes and detergents | Alkyl phenol-ethoxylate Triethanolamine Diethanolamine: <1% | Surfactant Inhibitor Inhibitor |

b. Textile products for golden objects

| Tekstilprodukter | | | |
|-----------------------------|--------------------------|-------------------------|-----------------------|
| Product name | Ingredients on packaging | Ingredients according | Ingredients' function |
| | | to data sheet | |
| Connoisseurs Jewelry Wipes | None | No dangerous substances | - |
| Connoisseurs Gold Jewellery | Cotton fibres 100 % | No data sheet | - |
| Polishing Cloth | | | |

The two products purchased to clean gold through dipping are based on:

- surfactants which can remove grease and dirt
- inhibitors
- organic solvents which quickly evaporate leaving a glossy glow
- perfume and pigments.

It is not possible to obtain information about the content in impregnated textile products for gold and jewels in general. On the available data sheet of one textile product it is also just stated that it does not contain dangerous substances.

3.2.2 Evaluation of product information on polishes for gold and jewels

Packaging information has been compared with the available information in the shape of formulations and data sheets. It was possible to obtain safety data sheets of all four products but no formulations.

3.2.2.1 Products for dipping

The packagings and safety data sheets of the two products for dipping golden objects do not quite agree. The packaging of one product informs about a row of substance groups, which are not mentioned in the safety data sheet, but they do not necessarily mean anything for the classification of the product. On the other product the labelling on the packaging is ambiguous "No pigments, harmful perfumes and detergents", as it can mean that there are no harmful detergents in the product or that there are no detergents in the product. Therefore, it is impossible to evaluate if the information on the packaging and in the safety data sheet agree.

3.2.2.2 Textile products

The packagings and safety data sheets of both impregnated cloths state that the products are not dangerous.

3.3 Cleaning materials and polishes for copper/brass

Information has been gathered on four products which can be used as polishes for objects of copper and brass. Cloths are to be used in connection with all four products, and they are sold as viscous, creamy products. Information on the internet show that the same suppliers also deliver

impregnated cloths and gloves to pollish copper and brass, but these products were not found in the shops visited.

3.3.1 Content of chemical substances in polishes for copper/brass

The purchased polishes for copper/brass are listed in table 3.3 a below. The table contains information about trade name, ingredients mentioned on the packaging and mentioned in the supplier's/manufacture's safety data sheets and finally the function of ingredients.

Table 3.3 a. Creamy products for copper/brass

| Creamy products | | | |
|--|--|--|--|
| Product name | Ingredients on packaging | Ingredients according to data sheet | Ingredients' function |
| Sterling kobber og messing beskytter og pudsemiddel | White spirit | White spirit: 30-100% Ammonium: 1-5% | Solvent Inhibitor |
| Sterling Bistro Kobber og messing Rensecreme | None | Citric acid: 10-30% | Inhibitor |
| Brasso | White spirit | Solvent naphtha (petroleum) medium aliphatic: 60-80% Ammonia water: <0,1% | Solvent Inhibitor |
| Hagerty Copper polish | Detergent Solvent Anionic tensides Corrosion protection Thickener Perfume Accessory agents | No data sheet | Detergent Solvent Surfactant Inhibitor Thickener Perfume |

The following ingredients were found in the four products for polishing copper/brass:

- surfactants which can remove grease and dirt
- abrasives/polishes which ease cleaning
- inhibitors
- organic solvents which quickly evaporate leaving a glossy glow
- polymers to make the products more viscous
- perfume and pigments.

All products contain some of these substance types.

3.3.2 Evaluation of product information on polishes for copper/brass

The information on the packaging is compared with the information available in the shape of formulations and data sheets.

It was possible to obtain safety data sheets on three of the four products and formulations of two products. Information on products, for which there are safety data sheets and formulations, agrees well with the information on the packaging.

Judging from the labelling there is a difference in the harmfulness of the products, as two of the products are classified as harmful and the packaging is labelled with tactile warning.

3.4 Cleaning materials and polishes for steel and other metals

Information has been gathered on three products which are sold to clean and polish metal surfaces in for instance kitchens. The products were found at ironmongers and convenience stores. According to the information on the packaging these three products can be used on all types of metal surfaces.

3.4.1 Content of chemical substances in polishes for steel and other materials

The polishes purchased for steel and other metals are listed below in table 3.4 a. The table contains information about trade name, ingredients mentioned on the packaging and ingredients mentioned in the supplier's/manufacture's safety data sheet and finally the function of the ingredients.

Table 3.4 a. Creamy products for steel and other metals

| None Anionic tensides: < 5 % Citric acid Polish Alcohol | Ingredients according to data sheet No data sheet No data sheet | - Surfactant Inhibitor Polish |
|--|--|--|
| Anionic tensides: < 5 % Citric acid Polish Alcohol | | Inhibitor |
| Citric acid Polish Alcohol | No data sheet | Inhibitor |
| Polysaccaride | | Solvent Thickener Perfume |
| Distilled water Aluminium oxide Alkylbezosulphate Glycerin-monostearate: -5% Oleic acid: -5% Triethanolamine: -5% Ethoxylatalcohol: -5% Phosphoric acid: 2% | Water Silltin 85 Sodiumdodecyl-benzene sulphonate Glycerolmonostearate Oleic acid Triethanolamine Fatty alcohol ethersulphate Phosphoric acid Calcit | Solvent Polish Surfactant Polish Wax Inhibitor Surfactant pH-adjustment Polish |
| | Perfume Distilled water Aluminium oxide Alkylbezosulphate Glycerin-monostearate: -5% Oleic acid: -5% Triethanolamine: -5% Ethoxylatalcohol: -5% | Perfume Distilled water Aluminium oxide Alkylbezosulphate Glycerin-monostearate: -5% Oleic acid: -5% Triethanolamine: -5% Ethoxylatalcohol: -5% Phosphoric acid: 2% Water Silltin 85 Sodiumdodecyl-benzene sulphonate Glycerolmonostearate Oleic acid Triethanolamine Fatty alcohol ethersulphate Phosphoric acid |

The three products for steel and other metals are treated separately, as the description on the packagings mentions different uses.

One product can be used to clean all metal surfaces in kitchens.

The second product can be used for stainless steel, copper, brass, chromium, tin, gold, aluminium, enamel, etc. not just in households but also for cars, boats and the like. Pictures on the packaging show cutlery, pots, jugs and other metal objects, which have to be polished.

The third product is recommended for kitchenware and can be used for other metal surfaces like eg. nickel, chromium, copper, brass and enamelled surfaces.

The following substance groups are represented in the three products for polishing steel and other metals:

- surfactants which can remove grease and dirt
- abrasives/polishes which ease cleaning
- faint acids which can remove lime and some metal oxides
- · organic solvents which quickly evaporate leaving a glossy glow

- wax or the like which may form a protective film hindering the oxygen from the air to get to the surface
- perfume.

All products do not contain all of the above, and therefore it is not possible to compare the compositions of the products.

3.4.2 Evaluation of product information on polishes for steel and other metals

Information on the packaging has been compared with available information in the shape of formulations and data sheets. It has been possible to procure formulations of all three products but only safety data sheet of one product.

Information on the packaging and obtained information agree well for the three cleaning materials and polishes.

4 Review of DIY-recipes and products

4.1 Recipes of DIY-products

Through searches on the Internet a row of recipes were found of how to mix your own cleaning materials and polishes on the basis of pure substances. Furthermore, leaflets from druggists contain recipes.

4.1.1 Silver

Two recipes were found to clean silver objects.

4.1.1.1 Recipes

Silver 1:

A pot is lined with aluminium/tin foil and a mixture of one decilitre common salt (sodium chloride) and one litre boiling water is poured into the pot. The silverware is dipped into the mixture for 20-30 seconds and rinsed in cold water and dried off with a soft cloth.

Silver 2:

Place two spoons of soda ash in a tub with one litre of water and a piece of aluminium foil. The silverware is placed in the tub for two minutes and is dried off with a cloth. There is a warning not to use it for oxidised silver. This warning is a little special, as the purpose of the recipe is to remove oxidised silver, but as many jewels consist of oxidised silver in a grey tone, and they are supposed to look like this, it is a warning that this silver will be shiny/glossy.

4.1.2 Gold

Two recipes have been found to clean golden objects.

4.1.2.1 Recipes

Gold 1:

Pour boiling water over washing-up liquid and a drop of household ammonia. Place the gold in the mixture for approx. one minute. Can be scrubbed with a toothbrush. Rinse with cold water and then dry it off with a soft cloth.

One part vinegar and one part lukewarm water are mixed, and the object is carefully dried with a cloth dipped in the mixture. There is a warning that gold may be many things, and therefore it is recommended to go carefully about it. The vinegar mixture is a mild product.

4.1.3 Copper/brass

Two recipes were found of polishes to clean copper and brass objects.

4.1.3.1 Recipe

Copper 1:

One part sulphuric acid is mixed with seven parts water and the copper object is washed in it. Rinse the object carefully with water.

It is also informed that it is dangerous to work with sulphuric acid and that the mixture is to be regarded as chemical waste which has to be delivered to a recycling centre.

Copper and brass 1:

A few drops of citric acid is mixed with a few drops of washing-up liquid stirred into lukewarm water. The brass object is dipped into the liquid for a couple of minutes and is then rinsed with plenty of water.

A somewhat more detailed recipe, in which it is recommended to use a brush by application, contains a solution of two spoons citric acid in one litre water with a few drops of washing-up liquid.

4.1.4 Other metals

A recipe has been found which can be used for other metals than the ones mentioned above, viz. to clean aluminium.

4.1.4.1 Recipes

Aluminium 1:

Methylated spirits can be used to polish aluminium - perhaps in a mixture with Paris white.

4.2 The function of chemical substances

The above DIY-recipes generally contain the same chemical substances which are found in ready-to-use products. However, the method to clean silver with aluminium, in which the potential of different metals in the galvanic electrochemical series is used, is not used in connection with the available ready-to-use cleaning materials and polishes.

The following pure substances are used:

- Citric acid
- Ammonia
- Acetic acid
- Sulphuric acid
- Sodium chloride
- Carbonate of soda (anhydrous sodium carbonate)
- Spirit (ethanol)
- Calcium magnesium oxide (Paris white)

Most of these substances take part in a chemical process with metal surfaces, viz. citric acid, ammonia, acetic acid, sulphuric acid, sodium chloride and carbonate of soda (sodium carbonate). As solvents only spirit (ethanol) and water are mentioned.

5 Survey of individual substances and substance groups according to their function

In this chapter the various types of substance groups are mentioned on the basis of their function in cleaning materials and polishes. As some information is obtained from formulations, which have to be kept confidential, the precise chemical name of some substances cannot be mentioned, but wherever possible a description as precise as possible will be used. Furthermore, the concentration of some substance groups cannot be stated precisely either due to missing information or confidentiality. Therefore, specific concentrations are not mentioned but instead typical concentration intervals are stated.

5.1 Surfactants

Surfactants have a cleaning effect on the surfaces from which they remove grease and dirt. The removal of grease and dirt means that other substances can more easily remove metal oxides on the metal surface.

In this project the following surfactants were found:

- Ethoxylated fatty alcohols (C12-14)
- Alkyl phenolic ethoxylates
- Fatty alcohol polyglycolether (nonionic tenside)
- Anionic tensides
- Alkyl benzosulphate
- None-defined surfactants.

The typical concentration of surfactants in the products is $1\,\%$. One single product contains 5-10% surfactants.

Generally, surfactants irritate and degrease skin and eyes. Anionic tensides are generally more irritating than nonionic tensides. Tensides strain the external environment, and especially alkyl phenolic ethoxylates are unwanted because of the accumulation of breakdown products in waste water sludge among other things.

5.2 Abrasives/polishes

Abrasives are added to cleaning materials and polishes to give a physical effect on the metal surface. When polishing with abrasives dirt and metal oxides are more easily removed as the abrasives supplement the chemical effect of other substances.

In this project the following abrasives were found:

- Quarts
- Kaolin (aluminium silicate)

- Aluminium oxide
- Calcium magnesium oxide
- Non-defined polishes.

The content of abrasives and polishes varies a lot. The dipping-products do not contain any polishes at all, whereas the creamy products contain 10-30% abrasives.

Abrasives irritate skin and eyes and are also irritating in connection with inhalation of dust. Furthermore, respirable quartz may also cause cancer. Abrasives and polishes do not immediately present any danger to the environment.

5.3 Brighteners/inhibitors

The function of brighteners is to make a protective surface on clean metal surfaces typically by co-ordinating a link with the metal surfaces.

In this project the following complexing agents were found:

- Thiourea (CAS-no. 62-56-6)
- Triethanolamine (CAS-no. 102-71-6)
- Diethanolamine (CAS-no. 111-42-2)
- Sodium EDTA (CAS-no. 64-02-8)
- Ammonia (CAS-no. 7664-41-7)
- Citric acid (CAS-no. 77-92-9).

Typically the products contain 1-5% brighteners, but one product contained as much as 16.5 % brightener.

The inhibitors mentioned all irritate skin and eyes. Inhalation of ammonia seems irritating or corrosive to airways depending on the concentration. Thiurea is classified as harmful and suspected of being both carcinogenic reproduction toxic as well as dangerous for the environment. Diethanolamine is under the suspicion of damaging the liver. EDTA is suspected of being reproduction toxic.

5.4 Organic solvents

The organic solvents have a fat-soluble effect on the surface and thus they clean the surface. At the same time they evaporate quite fast and leave a shiny look.

In this project the following organic solvents were found:

- Ethanol (CAS-no. 64-17-5)
- 2-Propanol (CAS-no. 67-63-0)
- Naphtha (petroleum), hydrodesulfurised heavy
- 2-butoxyethanol ((CAS-no. 111-76-2)
- Solvent naphtha (petroleum) medium aliphatic (turpentine) less than 0.1% benzene.

The content of organic solvents varies a lot in the products. There is information about concentrations of 5-20%, but some products contain as much as 60-80%.

Organic solvents irritate and degrease skin. Inhalation of high concentrations of vapours irritates the respiratory system and may give headaches, dizziness and discomfort. Prolonged or repeated exposure to high concentrations may damage the central nervous system.

Furthermore, ethanol, propanol and turpentine are flammable, but only in two cases the concentration is so high that it represents a fire risk (white spirit).

None of the organic solvents are classified as dangerous for the environment.

5.5 Acids/bases

Acids and bases are added to the cleaning materials and polishes to stabilise them. Furthermore, acids and bases are used in some products to dissolve metal oxides.

In this project the following acids/bases were found:

- Sodium hydroxide (CAS-no. 1310-73-2)
- Sulphuric acid (CAS-no. 7664-93-9)
- Hydrochloric acid (CAS-no. 7647-01-0)
- Phosphoric acid (CAS-no. 7664-38-2)
- Sodium carbonate (CAS-no. 497-19-8)
- Acetic acid (CAS-no. 64-19-7).

The content of acids and bases in the products is typically 1-10%, but sulphuric acid is used concentrated in one of the DIY-products.

Concentrated acids and bases are mostly corrosive, but sodium carbonate is irritating. However, in the concentrations in which they are present in the cleaning materials and polishes they are diluted, so they may seem irritating by skin and eye contact given that they do not react chemically with other substances. However, sodium hydroxide is corrosive in concentrations as low as 2%. Acids and bases do not directly present any danger to the environment.

5.6 Wax

Wax is added to cleaning materials and polishes to make the metal objects shine after polishing and to protect the surface against the oxygen of the air.

In this project the following waxes were found:

Non-defined wax.

Neither the type nor the concentration of the wax is available in this project and therefore, the harmfulness of the wax cannot be described.

5.7 Thickeners

Thickeners are added to make the cleaning materials and the polishes more viscous. Thickeners are especially added to products which are supposed to

be used with a sponge or a cloth. The purpose is to prevent that the product squirts and runs of the surface.

In this project the following thickeners were found:

- Cellulose powder
- Hydroxyethylcellulose
- Xanthan gum
- Polysaccharides
- Non-defined thickeners in the shape of polymers.

Thickeners are normally added in the concentrations 1-5%.

Thickeners are not regarded as having any harmful characteristics or being dangerous for the environment.

5.8 Preservatives

For some of the aqueous cleaning materials and polishes it is stated that preservatives are added. The preservatives are solely added to ensure the durability of products after they have been opened.

In this project the following preservatives were found:

- Isothiazolinones
- Formaldehyde-dissociating preservative.

It is not necessary to add preservatives in high concentrations to make them work, and there is information about concentrations less than 0.001%.

The preservatives mentioned may be allergenic. In high concentrations they may also irritate skin. Some isothiazolinones are already classified as dangerous for the environment.

5.9 Wetting agents

Substances which makes it easier for other substances to attach metal surfaces may be added to cleaning materials and polishes. These are called wetting agents.

In this project the following wetting agents were found:

- Propylene glycol (CAS-no. 57-55-6)
- Glycerol (CAS-no. 56-81-5).

These substances are added to the products in concentrations of 1-5%.

Propylene glycol and glycerol are not regarded as being harmful or dangerous for the environment.

5.10 Perfume and dye

Perfume may be added to cover an unpleasant odour from cleaning materials and polishes or of cosmetic reasons. Dye in cleaning materials and polishes are only added of cosmetic reasons.

In this project the following perfumes and dyes were found:

- Non-defined perfumes
- Non-defined dyes.

Perfumes and dyes are added to the products in concentrations less than 1%.

Many perfumes are allergenic by skin contact, whereas it is not possible to describe the harmfulness of the dyes in general.

5.11 Accessory agents

Accessory agents may be added to support the function of other chemical substances or to ease the solubility of other chemical substances.

In this project the following accessory agents were found:

Sodium chloride (CAS-no. 7647-14-5).

In one product to which sodium chloride has been added the concentration is 1-5%.

Sodium chloride (common salt) is regarded as being neither harmful nor dangerous for the environment.

6 Conclusion

6.1 Availability of cleaning materials and polishes

As a consumer it is possible to find products to clean and polish metal objects in convenience stores as well as specialist shops. The supply seems to be largest within cleaning materials and polishes for silver in the specialist shops.

Internet searches and visits to the shops gave the same picture of the availability of products on the market. Therefore, it is evaluated that the mapping has covered the market satisfactory.

6.2 Quality of information gathered

Cleaning materials and polishes are chemical products comprised by the regulations within labelling and classification. This means that it has to be mentioned on the packaging if the product is dangerous.

Information has been gathered on three levels:

- Informative labelling of the packaging
- Safety data sheets
- Formulations.

For the products sold in convenience stores packaging information and safety data sheets were available in Danish. Information on the products in specialist shops was different, as the main part of information on these products was not in Danish.

To be able to evaluate if a product is dangerous you need to have access to the complete formulation of the product. It was impossible to obtain formulations on all products and therefore, it was not possible to evaluate if all pieces of information on the packagings were correct. However, in connection with the available formulations in this project, information on the packaging and the classification in the formulations agree.

Safety data sheets are normally not available to the ordinary consumer, as lawfully they only have to be handed out when a product is to be used at a workplace. Furthermore, there is no requirement for safety data sheets of products which are not classified (with a few exceptions). In this project information from safety data sheets have been used if it was not possible to obtain formulations.

It has been possible to obtain the following pieces of information on 25 of the examined ready-for-use products.

The packaging of 19 of the 25 products had an informative label. Some of the informative labels are so detailed that they are like incomplete formulations. It was possible to procure safety data sheets on 16 of the 25 products. We obtained access to 13 formulations and evaluated that six of these were incomplete.

6.3 Evaluation of ingredients

Based on the different functions of ingredients in a cleaning material or polish it is evaluated that generally there are no redundant substances in the ready-for-use products. However, it should be possible to leave out dyes and perfumes, as they do not have any effect on the efficiency and function of the products.

When going through the ingredients a few very suspicious substances were found. Thiourea is classified as harmful and dangerous to the environment in addition it is suspected of being carcinogenic (carc3) and reproduction toxic (rep3). The four products that contain this substance have to be classified with at least R40 (Possible risk of irreversible effects). There are alternative products, which can solve the case but this would require more time and effort by the user.

Several products contain preservatives of the type isothiazolinones and formaldehyde-split off substances. Both substances are alarming, as they are evaluated as being allergenic, even though they only appear in small quantities in the products.

Nonylphenolethoxylates, which are unwanted in the environment, should be emphasised. In other connections it has been possible to substitute these tensides with less environmentally harmful alternatives. Within the tenside area many tensides are accessible today, which are far less environmentally harmful than nonylphenolethoxylates eg. sugar tensides.

The recipes of DIY-agents do not prescribe the use of some of the above mentioned problematic substances. In return the use of a sulphuric acid, which is strongly corrosive, is prescribed. It is alarming that the user has to handle a corrosive substance like sulphuric acid to make cleaning materials and polishes, and then dispose of it as dangerous waste. The consumer should carefully consider if he can protect himself and the environment sufficiently, or if he has to use a less risky method and use one of the mentioned products instead.

The possibility to substitute the above with less dangerous substances exists.

6.4 Efficiency

In this project the efficiency of the products has not been evaluated. It has also not been examined how long the polishing lasts. Other things being equal it will be a matter of opinion and depend on the exposure of the metals. Some products are stated as being long acting whereas daily use is recommended of other products (especially products for jewels).

6.5 Eco-labelling

At present it is not possible to obtain an eco-label on a cleaning material or polish as criterions have not been lay down.