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Dermal exposure due to airless spray painting -a semi-experimental study during spray painting of a container

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Samenvatting

In deze studie is onderzoek gedaan naar het voorkomen van huidblootstelling bij het spuiten van verf. Na een pilot-studie werd besloten een onderzoek te starten in de off-shore industrie, waar de airless spuittechniek gebruikt wordt. Het belangrijkste doel van de studie was het vinden van de range van huidblootstelling aan vaste stof bestanddelen uit verf tijdens het airless verfspuiten. Daarnaast is gekeken in hoeverre de gevonden blootstelling overeenkomt met de schattingen gemaakt met behulp van het blootstellingsmodel EASE.

Huidblootstelling werd gemeten in drie verschillende off-shore bedrijven tijdens het airless spuiten van een zelfde container. Door de verf werd een fluorescerende stof (tracer) gemengd (de concentratie van de tracer in verf was 0.0074% w/w), waarna met behulp van het VITAE systeem (Video Imaging Technique for Assessing Exposure) de hoeveelheid tracer op de coverall en op de onbedekte huid van de spuiters gekwantificeerd kon worden.

De resultaten laten depositie van verfnevel zien tijdens het airless verfspuiten. Ondanks de experimentele opzet van het onderzoek (één object, één spuittechniek) is de variatie in de dermale blootstelling aanzienlijk (variërend van 2 tot 806 µg en van <0.01 tot 52 µg tracer op de coverall en de huid respectievelijk). Als deze gegevens worden gebruikt in het kader van het kennisgevingsstelsel, dan betekent dit voor een niet-vluchtige stof die voor 10% in verf voorkomt, dat de volgende blootstellingsranges berekend kunnen worden

handen en hoofd:	<0.02-70 mg.
coverall:	3-1090 mg.

De invloed van de hoeveelheid verf, en de duur van het spuiten op de blootstelling is geanalyseerd met behulp van lineaire regressie. Na het uitsluiten van de gegevens van één persoon, werd een significante relatie gevonden voor beide factoren en de coverall blootstelling, terwijl voor de blootstelling op de blote huid alleen een relatie werd gevonden tussen blootstelling en hoeveelheid verspoten verf. Naast deze factoren is de persoonlijke werkwijze van groot belang. Ondanks dat een aantal van deze factoren (manier van spuiten, afstand tot het object) is beoordeeld in het onderzoek, kon geen van de variabelen aangewezen worden als blootstellingsbeïnvloedende factor.

Uit het onderzoek komt naar voren dat bepaalde delen van het lichaam hoger zijn blootgesteld dan andere. De resultaten van het onderzoek laten zien dat de onderbenen het hoogst blootgesteld zijn: na het spuiten van de buitenkant van de container zit 54% van de totale blootstelling op de onderbenen, na het spuiten van de binnenkant is dit 48%. De blootstelling van de handen van de spuiters is opvallend laag (ca. 3%), vooral in vergelijking met resultaten gevonden in de literatuur met betrekking tot het verspuiten van bestrijdingsmiddel.

Met behulp van het VITAE systeem kon tevens aangetoond worden dat het grootste gedeelte van de blootstelling optreedt op een klein deel van het totale oppervlak. Gemiddeld 13% en 7% van de coverall is detecteerbaar blootgesteld na het spuiten van de binnen- en buitenkant van de container. Voor de huid is dit percentage vergelijkbaar: 11% na het spuiten van de binnenkant en 12% na het spuiten van de buitenkant. Deze resultaten geven aan dat bij de risico-schattingen niet mag worden aangenomen dat (belangrijke delen van) het lichaamsoppervlak homogeen blootgesteld is.

Als de gevonden blootstelling wordt vergeleken met de schatting gemaakt met EASE, lijkt EASE een extreme overschatting te geven (maximale blootstelling berekend op handen en hoofd na extrapolatie naar een tracer concentratie van 10% in verf is 70 mg; EASE schat een blootstelling variërend van 300-900 mg/dag). Een van de kanttekeningen die bij deze vergelijking gemaakt kan worden is dat EASE een daggemiddelde blootstelling schat en het onderzoek een blootstelling over maximaal 21 minuten heeft gemeten. Om een betere vergelijking te kunnen maken tussen de schatting gemaakt met EASE en de resultaten van het onderzoek, wordt de blootstelling op de huid en de handen, berekend op basis van een 10% tracer concentratie in verf, nog eens geëxtrapoleerd naar een 3 uur durende blootstelling. Dit resulteert in een blootstelling van 540 mg (berekend op basis van de 90 percentiel waarden verkregen uit het onderzoek) hetgeen binnen the range van de EASE-schatting valt. Aangezien ongeveer 95% van de totale potentiële blootstelling gemeten is op de coverall, is het zeer goed mogelijk dat een gedeelte daarvan door penetratie door de coverall of door 'lekkage' langs de coverall op de huid (anders dan het hoofd en de handen) terecht komt.

Hoewel er enige onzekerheid bestaat over de extrapolatie (naar gebruikte hoeveelheid en tijd) van de meetgegevens, is er op dit moment geen aanleiding de schatting met behulp van EASE aan te passen. Aanbevolen wordt een studie op te starten waarbij zowel meer tracer in de verf aanwezig is als gedurende een langere periode te spuiten.

Summary

In this study dermal exposure by spray painting has been investigated. After a pilot-study it was decided to start a study in the off-shore industry, where the airless spray painting technique was used. The main purpose of the present study was to determine the range of potential dermal exposure to paint during airless spray painting. It was also investigated whether the observed exposure corresponds with the estimates made by the exposure model EASE.

Skin exposure was measured in three off-shore enterprises where a similar container was painted with use of the airless spray painting technique. A fluorescent tracer was mixed with the paint (concentration of tracer in paint was 0.0074% w/w). With use of the Video Imaging Technique for Assessing Exposure (VITAE System) the amount of tracer was quantified on the clothing and the uncovered skin of the painter.

The results show deposition of the paint spray due to airless spray painting. In spite of the semi-experimental setting of the study (one object, one spray painting technique) the variation in the potential dermal exposure is notable (ranging from 2 to 806 and from <0.01 to 52 µg tracer on the coverall and the skin respectively). Using these data in view of the new and existing substance regulation, and assuming a non-volatile substance concentration of 10%, the following exposure is calculated:

dermal exposure (face and hands): <0.02-70 mg

dermal exposure (coverall): 3-1090 mg.

The influence of the spray volume and of the duration of painting was analysed with use of linear regression. After excluding the exposure of one person both factors appeared to be significant related to the coverall exposure, whereas for the skin only the spray volume showed to be an exposure modifier, duration did not. The personal work-method of the painter might cause the additional variation in exposure. This could not be proven in the study, in spite of the investigation of some of them (spraying method, distance between painter and the container).

The results of the study show that some parts of the body are exposed more than other parts. The lower legs have the highest exposure: 54% of the total dermal exposure after painting the outside of the container, 48% after painting the inside of the container. The total exposure on the hands of the painters is relatively low (ca. 3%), compared to the results in the literature on pesticide application.

From VITAE analysis it also appeared that most non-volatile compounds deposit on a rather small percentage of the total body area. On average only 13 and 7% of the area of the coverall is exposed after spraying the in- and outside of the container. For the skin this percentage is comparable: on average 11% after spraying the inside of the container and 12% after spraying the outside of the container. This observation might have implications for the assessment of dermal exposure by applying models, which often assume total exposure of the total surface area.

When the results of the study are compared with the estimate made by EASE, it appears that EASE overestimates the exposure extremely (maximum skin exposure (hands) extrapolated to a tracer concentration of 10% in paint is 70 mg, while EASE estimates an exposure ranging from 300 to 900 mg/day). However, some remarks can be made on this comparison. One of them is the fact that EASE estimates an exposure per day, whereas this study measured the exposure with a spray painting duration of up to 21 minutes (mean 10 min). To enable a better comparison between the estimates made by EASE, and the exposure measured in the study, the exposure will be extrapolated to both a 10% non-volatile substance concentration in paint and to a 3 hour exposure duration. This results in an exposure of 540 mg (calculated in view of 90 percentile values derived from the study), which fits into the range estimated by EASE. Since approximately 95% of the exposure is present on the coverall, actual exposure may occur of covered parts of the skin either by penetration through the coverall or through leakages.

Although there is some uncertainty on the extrapolation (to spray volume and time of spray painting) of the measured data, it appears that at the present moment there is no reason to adjust the exposure estimate made by EASE. It is suggested that a study should be emphasized at a higher tracer concentration in paint, and a higher spray painting duration.

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1. Introduction

To assess the risks for workers from exposure to chemicals, the assessment of occupational exposure on a screening level is an important element. To estimate dermal exposure two models are available: the model of the US Environmental Protection Agency (US EPA) and the model of the UK Health and Safety Executive (UK HSE), which was derived from the US EPA model (TGD, 1996). Both the US EPA model and the EASE model are based on experiments and not on knowledge of actual occupational skin exposure. In the risk assessment on new and existing substances under European Regulation (Commission Directive 93/67/EEC and Council regulation No. 793/93) the EASE model is used (see appendix A) by The Netherlands. A study has been conducted to obtain dermal exposure data in a typical industrial situation which enables comparison of data with estimations by models.

The selection of the industry and the activity for the study was based on the following conditions.

- the industry/activity had to be relevant in view of the exposure assessment of ‘new and existing substances’ (in the scope of European regulations: Commission Directive 93/67/EEC and Council regulation No. 793/93);
- in the process there had to be strong evidence for dermal exposure;
- the frequency of the activity had to be high enough (*e.g.* activities which are performed only accidentally are with respect to this investigation less interesting);
- the activity must occur in different industries, so an extrapolation can be made towards other industries;
- The method of detection of the substance may not be too complicated.

Based on the above mentioned criteria a choice was made to perform a dermal exposure study during spray painting activities. Spray painting is an activity which is performed frequently, and in different industries (*e.g.* metal, aircraft and furniture industry). First a pilot study was performed to decide what technique is the most important, in view of the dermal exposure. The results of the pilot study and the main study performed afterwards in the off-shore industry are described in this report.

1.1 Aim of the study

The main purpose of the study was to determine the range of potential skin exposure to paint during airless spray painting.

Preliminary to the main study a pilot study was performed in which it was studied which spray painting technique (airless or pneumatic) and which object (a closet or the boards and the door of the closet) had the highest exposure. A rough comparison resulted in the decision to start a semi-experimental study on dermal exposure by airless spray painting of a relatively huge object.

The study addresses the following questions:

- what are the statistical distribution parameters (range, arithmetic mean, geometric mean, standard deviation, geometric standard deviation, minimum, maximum, 10th and 90th percentile) of potential dermal exposure to paint during spray painting in a semi-experimental setting?
- which percentage of the total surface area is exposed after spray painting and how is the contamination distributed over the body?
- is the dermal exposure and the dermal area dose, as it is found in this study, comparable to what is estimated by the EASE model, that estimates a dermal area dose ($\text{mg}/\text{cm}^2/\text{day}$)?
- is the dermal exposure different for two situations (spraying the in- and outside of the container)?

In addition:

Can determinants of dermal exposure be identified for this semi-experimental setting, *e.g.* duration of spray painting and spray volume?

In the following chapters a review of the relevant literature is given, together with the study design, the results of the exposure measurements, the discussion, conclusion and recommendations.

2. Spray painting

2.1 Introduction

Spray painting is one of several application techniques for paint. During spray painting the paint is dispersed in the direction of the object. The spray can be generated by compressed air, by hydraulic pressure or by electrostatic forces (O'Brien and Hurley, 1981). Some spray painting techniques are outlined in appendix B. The dermal exposure is mainly caused by back bouncing, which is a part of overspray. The process of overspray will be outlined below.

2.2 Overspray

Dependent on the spray painting application, some of the paint will not reach the object, but will deposit aside the object or will be reflected from the object, called 'back bouncing'. This part of the spray is called 'overspray'. Overspray is the mass sprayed, minus the mass that deposits on the object. Overspray leads to losses of paint and to pollution of the environment and it must therefore be prevented.

Paint particles of sufficient mass are not reflected and deposit on the object. Hama and Bonkowski (1970, referred to by O'Brien and Hurley, 1981) noted that droplets with a diameter less than approximately 12 micrometer are of insufficient mass to deposit on the object, and are therefore being reflected. They noted that approximately 20 percent of the droplets in pneumatic spray painting are smaller than 12 μm . During airless spray painting, the paint particles have a lower velocity when they leave the orifice than with pneumatic spray painting. Since only 2 percent of the spray droplets in airless painting are less than 12 μm , higher deposition efficiency are reported (approximately 65 - 70%) and therefore, less overspray is expected by using the airless spray painting technique compared to the pneumatic spray painting technique (Hama and Bonkowski, 1970, referred to by O'Brien and Hurley, 1981, Groenewoud, personal communication, 1996). With electrostatic spray painting there is little overspray because the paint particles are attracted by the grounded object (Heesen and van Raalte, 1994). In a publication by Evers (1987) an overspray-free spraying technique is introduced; a so-called low pressure turbine. The advantages of the overspray-free spraying technique are: less back bouncing, less haze and the fact that less paint has to be used to achieve the same thickness of paint. A disadvantage of the technique is a lower pace of work.

2.2.1 Influence of spray guns on overspray

Heitbrink *et al.* (1993) evaluated data on concentrations of paint in a downdraft spray painting booth to determine whether the type of spray painting gun affected total dust concentrations. This analysis was done because HVLP (high-volume, low-pressure) spray painting guns are reported to be more efficient than other types of spray painting guns (*i.e.* gravity feed and siphon cup pneumatic spray

painting guns). HVLP guns are assumed to have a transfer efficiency of at least 65%, while conventional spray painting guns are reported to have a transfer efficiency of 25 to 35% (Heitbrink *et al.*, 1995). Spray painting gun transfer efficiency is the ratio of the mass of paint solids that coat the surface to the mass of paint solids sprayed. Stationary (n=34) and personal (n=23) samples were collected. Sampling was performed during painting. The pressure in the nozzle of conventional (pneumatic) spray painting gun was between 3.5 and 4.5 bar. In the HVLP spray painting gun, atomization pressure was less than 0.7 bar. After adjusting for the effect of the duration of painting, it appeared that the total aerosol concentration for the HVLP technique was two times less than for the conventional spraying technique. However, this difference was not statistically significant (Heitbrink *et al.*, 1993).

In another study (Heitbrink *et al.*, 1994), the effect of the spray painting gun choice on solvent and particulate overspray concentrations was experimentally studied in a downdraft spray painting booth. Two spray painting guns were studied, a gravity-feed conventional (pneumatic) spray painting gun and a gravity feed HVLP spray painting gun. The pressure in the nozzle of the conventional spray painting gun was between 3.5 and 4.5 bar. In the HVLP spray painting gun, atomization pressure was less than 0.7 bar. During each experimental run, particulate overspray concentrations (mass concentration of paint solids), solvent concentrations, film thickness on the autobody and mass of paint used were measured. The sampling time varied between 12 and 25 minutes. The film thickness per mass of paint sprayed for the HVLP gun was 33 percent higher than what was observed for the conventional spray painting gun. This difference was statistically significant. Particulate overspray concentrations were measured as total aerosol concentrations by using personal sampling pumps. The conventional spray gun was associated with a particulate overspray concentration per unit of film thickness that was a factor two higher than with the HVLP spray gun. Again, this difference was statistically significant. The HVLP spray gun reduced the solvent concentrations by 21 percent, however, this was not statistically significant.

2.3 Health hazards in spray painting

Paint consists of several substances. The major categories are: binders (30-85%), pigments (0-30%), solvents (0-80%) and additives (0-35%). This holds for both solvent based paints and water borne paints. Binders are liquids, or solids in solution, in the paint formulation that become solid films either through solvent evaporation, coalescence, or a chemical reaction. Binders may be either natural (*e.g.* linseed) or synthetic (*e.g.* alkyds, acrylics, vinyls or urethanes) in origin. Pigments have several uses in paint, including opacity, colour, corrosion inhibition, reinforcement of the binder and general filler. Solvents in paint have several functions. They dissolve binder and/or make it more fluid. The solvent also functions to control viscosity for ease of production and application. They evaporate during painting and thus cause film formation. Sometimes water is used as a

solvent, but most binders only dissolve in organic solvents (aromatic hydrocarbons, aliphatic hydrocarbons, esters, ketones, glycol derivatives, alcohols or halogenated hydrocarbons). Additives are substances which are added to the paint in relative small amounts. They improve some characteristics of the paint or prevent unwanted characteristics. Softeners, preservatives, rust-preventers and siccatives are examples of frequently used additives. The exact composition of paint depends on the type of paint. The total amount of non-volatile compounds can run up to 80-90% of the total paint substances. Water borne paints and solvent based paints that contain relatively little solvent and have a percentage of solid substances of at least 85% are high solids (Peterson and Keller, 1989; Eysen *et al.*, 1992).

Because many substances of paint can be inhaled easily, after which they remain in the lung or are absorbed into the bloodstream, inhalation has been considered as the most significant route of entry for a long time. With the reduction of the airborne occupational exposure limits, the relative importance of the skin exposure route is increased (Fenske, 1993).

2.3.1 Dermal exposure

Fenske (1993) defined dermal exposure as the product of skin loading rate (mass per skin surface area per unit time) and area exposed (cm²). Dermal exposure in this context is expressed in units of mass per unit time (µg/h). Cherrie and Robertson (1996) proposed an alternative definition which recognizes the biological process involved in skin absorption, *i.e.* the concentration of the substance at the skin surface.

Dermal exposure can be distinguished in potential and actual dermal exposure. Potential dermal exposure is the total exposure of an individual, including the exposure of the clothing. The actual dermal exposure is the amount on the skin, either directly or after penetration of the clothing (Brouwer *et al.*, 1995). The undamaged skin gives some protection against the penetration of injurious substances. Nevertheless, some substances can penetrate the skin because of their own qualities or because of the qualities of the substance in which they are dissolved (Arbeidsinspectie, 1986).

Dermal exposure assessment during spray painting is mostly emphasized on dermal exposure to paint solids (binders, pigments and additives). During the painting droplet evaporation proceeds concurrently with droplet transfer and transport. Overspray droplets decrease in size as the solvent fraction volatilizes. This change in size distribution affects the movement of the overspray and results in worker exposure to solvent vapours. The overspray, consisting of paint solids and unevaporated solvent, contributes most of the worker's total mass exposure (Carlton and Flynn, 1997). When the overspray reaches the skin of the worker, most of the solvents will probably have been evaporated while the paint solids remain.

There is hardly any literature about the relationship between spray painting, dermal exposure and health effects, except for some isocyanates. Hexamethylene diisocyanate (HDI) is widely used in polyurethane-based paints and varnishes and is reported to cause skin and eye irritation next to respiratory sensitization, asthma and reduced lung function (Maître *et al.*, 1993; Heitbrink *et al.*, 1995). To prevent dermal exposure, one has to make sure that the skin does not get in contact with harmful substances. Cleaning of the skin with solvents must be avoided and clothes have to be changed frequently. Washing the skin during and after work is very important (Arbeidsinspectie, 1986).

2.4 Dermal exposure measurement techniques

There are several techniques to assess occupational dermal exposure. These include direct methods, which measure the mass of contaminant that is actually deposited onto the worker's skin or clothing, and indirect methods, like biological monitoring and the measurement of the mass of contaminant that is on the work surface. With direct measurement methods, quantification of most contaminants on the skin itself appears not to be feasible. A solution is sought intuitively in using sampling devices like surrogate skin, removing contaminants from the skin and the use of tracers to mimic the contaminant (Bierman *et al.*, 1995; Van Hemmen and Brouwer, 1995; Fenske 1993; Mc Arthur 1992). A review of the methods mentioned above is given in appendix C.

For the present study it was decided to use a tracer for assessing dermal exposure. The composition of paint is generally very complex, it is therefore very difficult to select a substance to be measured. At the moment of this study there are several difficulties for measuring solvents on the skin, *e.g.* solvents evaporate from the skin. Solid substances vary among different paints, therefore it was decided to use a tracer for assessing dermal exposure. To analyse the tracer the VITAE (Video Imaging for Assessing Exposure) system is used.

3. Materials and methods

3.1 Study design

3.1.1 Pilot study

First a pilot-study was executed, to determine which spray painting technique (airless or pneumatic spray painting) and what object (closed structure or open structure) would be most important with respect to dermal exposure. The pilot study was performed on three successive days in a spray test facility of a paint manufacturer.

In the pilot study two spray painting techniques were compared: the airless and the pneumatic spray painting technique. Two painters were involved in the study. Two objects were painted with both the pneumatic and the airless spray painting technique. The objects to be painted were a closet, which was the closed structure and the boards and the doors of the closet, which were meant to be the open structure.

Both techniques had to be applied for at least six times on the closet and for about three times on the boards (it was expected that the exposure was highest during painting the closet). If possible, every painter had to spray both techniques and both objects to eliminate the variation between the spray painters. At day one and two the closet was painted, while on day three the boards and doors of the closet were painted.

The results of the pilot study (chapter four) showed that skin exposure was highest after spraying with the airless spray painting technique, and that spraying a closed structure resulted in a higher exposure than spraying a subject with an open structure. With reference to the pilot study it was decided to start a study of the same kind in the off-shore industry. The reason to choose for the off-shore industry is that it is possible to spray large objects. From the results of the pilot study, it was expected that treating large objects would result in higher exposures than small objects.

Because mixing the fluorescent tracer with paint for commercial purposes is not desirable (the tracer might affect the colour of the paint), a semi-experimental setting for the study is chosen. The object to be painted is a container.

3.1.2 Main study

Skin exposure was measured in three off-shore enterprises to study the effect of different circumstances on dermal exposure. In each enterprise four spray painters painted the same object (a container of 36 m³), so the variation between persons could be observed.

The scheme of the painting was as follows:

- 3 enterprises;
- 4 painters per enterprise;
- each person paints the outside of the container two times.

Totally, the outside of the container was painted eight times per enterprise. The inside of the container was also spray painted several times. The measurements of one company were performed at two consecutive days in one week

From the pilot study it appeared that dilution and mixing of paint would result in unintentional exposure, therefore the paint was diluted (1:20; refined petrol:paint) and mixed by the investigators.

3.1.2.1 Additional observations

Although it was tried to perform a study with minimal variation, dermal exposure might be influenced by some factors. Therefore information regarding the following presumed modifiers was registered in the different enterprises:

- duration of activity;
- spray volume handled in the exposure period;
- pressure used;
- the distance between painter and container;
- orifice of the nozzle;
- control measures (such as local exhaust ventilation);
- working method of painter

Next to above mentioned modifiers, the temperature and air velocity in the workplace were measured with an anemometer (Alnor GGA-65). The distance between the painter and the container was estimated by the investigator. The way each painter painted was observed. It was registered whether the painter was spraying right- or left-handed, whether he was spraying with a vertical or a horizontal movement and whether he bended his knees or back during spraying. The latter factors (distance between painter and container and working method of painter) were analysed for another study, in which it was tried to develop a qualitative exposure model.

It was also tried to estimate the area exposed qualitatively by encircling the part which emitted light. This was done when the spray painter stood under UV light. In appendix D a sample of the standard registration form (in Dutch) is given.

3.2 Materials

The objects to be painted, a container (36 m³), and the closets were supplied by TNO. The used paint (Silvatane super vernis 'satin', Trimetal) was diluted with refined petrol (Elma, boiling point 100-140°C) in which the fluorescent tracer Uvitex OB (2.5-bis(5'-t.butylbenzoxazol-2-yl)thiofeen, CASno. 7128-64-5, CIBA-GEIGY) was dissolved. Uvitex OB was considered to be a good guidance compound for non-volatile compounds in paint. Originally, Uvitex OB is an UV absorbent/stabilizer for synthetic materials used in the food industry. The used concentration of Uvitex OB in the thinner was 1.4 g/l. During the airless spray

painting of the container the painters wore a Tyvek coverall (Tyvek-Pro-Tech, DuPont Engineering Products S.A., Luxembourg) and no gloves. The paint, the thinner, the tracer and the coverall were supplied by TNO.

3.3 Methods

With use of the VITAE technique dermal exposure to tracer is measured on the skin, and on the coverall. The methods and materials used are almost similar for the pilot study and the main study. There were some small differences, in the pilot study both the hands and the forearms were analysed and not the face, while in the main study exposure on the hands and the face was analysed. The forearms were not analysed in the latter study, because the results of the pilot study showed that the exposure on the forearms was negligible, due to the Tyvek coverall.

In the following the methods of the main study will be outlined. When different methods were used in the pilot study this will be mentioned.

Before and immediately after spray painting the object, VITAE images of the skin (hands and the head) of the painter were taken. The initial images had to be taken, since the amount of fluorescent light in an image is not only proportional to the amount of tracer on the skin, but also depends on the response of the skin itself. After spray painting, images of each coverall were analysed by the VITAE technique. Some coverall pieces were analysed chemically to check the relation between the chemical and the VITAE analysis.

After the object was sprayed, 10 images of the skin (five different sides, before and after spray painting) and 34 images of the Tyvek coveralls were made per person:

Locations of the body analysed:

- palm of the right hand;
- palm of the left hand;
- back of the right hand;
- back of the left hand;
- head.

Locations of the Tyvek coverall analysed:

- lower leg 4x (left, right, front and back);
- upper leg 4x (left, right, front and back);
- forearm 4x (left, right, front and back);
- upper arm 4x (left, right, front and back);
- hood 2x (left and right);
- torso 16x (8x front, 8x back).

Images were recorded using a camera (SDH0703/AS, Philips, Eindhoven, The Netherlands) and were digitized with a 'framegrabber' (DT2853, Data Translation, Marlboro, MA, USA) installed in a personal computer. Images digitized with this equipment consist of 512x512, 8 bits picture elements (pixels). This implies that, with a distance of 1 m between object and camera, each pixel covers an object area of 0,775 mm². Each pixel may have a value from 0 to 255, normally referred to as grey value of the pixel (Bierman *et al.*, 1995). For each pixel in an image of the skin the grey value of the 'before' image (= skin response) and of the 'after' image (= spot fluorescence) was determined. If the grey value of the 'after' image was at least one unit higher (limit of detection, LOD) than the grey value of the 'before' image, deposition of tracer was assumed to have taken place and the amount of tracer was estimated by inserting the skin response and the spot fluorescence values in the calibration curve. No exact value for the LOD could be given for the Tyvek coverall or for the skin. The relation between the amount of Uvitex OB on skin and the grey value of the pixel is linear until a grey value of circa 250. The relation between the amount of Uvitex OB on Tyvek and the grey value of the pixel is linear until a grey value of approximately 60. Images (or pieces of an image) with a grey value of more than 60 per pixel, could not be translated to the amount of Uvitex OB on Tyvek. These (pieces of) images were left out of the analysis. The range of quantification of Uvitex OB on a Tyvek coverall approximately lies between 30 and 250 ng/cm² (see appendix E). For Uvitex OB on human skin the range of quantification lies between 50 and 1000 ng/cm². The minimum quantifiable level were respectively 30 and 50 ng/cm² for coverall and skin. The amount of Uvitex OB on the coverall and on skin are given in absolute amounts (ng) per image. Also a dermal area dose is calculated (ng/mm²). This is performed by injunction of the exposure of all coverall parts divided by the exposed area. The calculated dermal area dose is compared with the exposure estimated by EASE (also given in mg/cm²/day).

3.4 Quality control

During the study, field blanks and field spikes were taken to study contamination and stability under influence of moisture, temperature and light of the guidance compound during fieldwork, transport and storage of the samples (SOP: DATV/AT/017 Taking samples in field studies to determine the source strength). Every sampling day two field spikes were taken, one low concentration spike (varying from 8 to 34 µg Uvitex OB in paint) and one high concentration spike (103 µg Uvitex in paint). Every sampling day, two blanks were taken which were analysed chemically. One of the blanks was spiked with paint without Uvitex OB and the other one was just a blank piece of coverall. Of one blank coverall VITAE analyses were made to determine the background of a coverall. Every time the container was painted, new paint was mixed with refined petrol (with the tracer) by the investigators of TNO. A sample of the paint used was taken every time new paint was mixed, to check the concentration of Uvitex OB in the paint. This sample was analysed chemically.

3.5 Chemical analysis

Not all coverall parts were analysed chemically. To enable chemical analysis of a coverall, the coverall must be stored in 11 pieces in jars with refined petrol before chemical analysis. For each enterprise one complete coverall and an additional back and front torso were analysed chemically (see appendix F). For the pilot study three complete coveralls were analysed. Forearms (left, right), upper arms (left, right), lower legs (left, right), upper legs (left, right) and hood were stored in 1 litre jars with 300 ml refined petrol. The torso of the coverall (front, back) was stored in a 2.5 l jar with 1.5 l refined petrol. The chemical analysis was performed by the laboratory of TNO.

Uvitex OB was extracted from the matrix (Tyvek) and analysed with use of fluorescence detection (excitation wavelength = 371 nm, emission wavelength = 425 nm). For the detection a Kontron SFM 25 detector was used. The calibration curve of Uvitex OB, dissolved in refined petrol, is linear until at least 2.2 mg/l. The limit of quantification of Uvitex OB is approximately 5 µg/l, while the limit of detection of Uvitex OB is circa 3 µg/l. This means a LOD of ca. 1 µg for the forearms, upper arms, lower legs, upper legs and hood, and a LOD of 4.5 µg for the torso.

The compound in the matrix, stored in extraction liquid at room-temperature, was stable for at least ten days. The compound in the extraction liquid, separated from the matrix and stored in the refrigerator, was also stable for at least ten days. When the Uvitex OB in paint was applied on the coverall and it was dried for three hours, the recovery was 100%. When the Uvitex in paint on the coverall was dried for four hours the recovery was 70%, but when, after this period, the coverall was stored for 24 hours in refined petrol the recovery was 100%.

3.6 Statistical processing of data

The software used during the study is Excel for Windows (version 7.0). With Excel both the database was made and the statistical analysis performed.

The statistical distribution parameters (range, arithmetic mean, geometric mean, standard deviation, geometric standard deviation, minimum, maximum, 10th and 90th percentile) of the total skin exposure and the total exposure on the Tyvek coverall were calculated. For the pilot study only the statistical distribution parameters on the skin and the total coverall were calculated. No other tests were performed on these data.

The statistical distribution parameters were also calculated separately for the three different workplaces. The analysis was done both for the exposure of the coverall and of skin together and for coverall and skin separate. The Mann-Whitney U test was used to study whether exposure is different between the workplaces.

The paired-sample t test was used to test whether there was a significant difference between the exposure after painting the outside of the container for the first and the second time (two sided). The same test was used to study whether there was a significant difference between the spray volume, and the duration of spray painting for painting the outside of container for the first and the second time. To test if the exposure is significantly higher after painting the inside of the container compared to the outside of the container, the Mann-whitney U test is used (one sided).

To study the distribution of the contamination over the body parts, the coverall was analysed in parts. Exposure of the head of the painter was measured on the coverall (hood) and on skin (face), these two measurements were summed. To study whether the exposure was distributed equally over the total surface area, the percentage of the area exposed, related to the total area was calculated (AM, SD and range). The analysis was done separately for skin and coverall, after spray painting the in- or outside of the object.

The Mann-Whitney U test was used to test whether there is a difference in exposure of the spray-hand compared to the hand which is not used to spray (non-spray-hand; one sided). The same test was used to study which part of the coverall was exposed highest: upper (hood, arms and torso) or lower (legs) part and front or back.

The exposure was calculated in absolute amount of Uvitex OB (ng), and in mg/kg Uvitex OB (the latter only holds for the total exposure).

3.6.1 Linear regression analysis

The influence of the duration of spray painting, the spray volume and the pressure was analysed by linear regression. The following model was studied:

$$\text{Skin exposure (mg/activity)} = c + \beta * \text{var}$$

in which:

- c : constant;
- β : regression coefficient;
- var : independent variable.

The square of the correlation coefficient (R^2) indicates the amount of variation in the dependent variable (skin exposure) explained by the independent variables (exposure determinants).

If a significant correlation between exposure and one of the mentioned potential exposure determinants was observed, the exposure unit might be standardized for the correlated factor (depends on the amount of variation in the dependent variable, explained by the independent variable; when this is too little). The other observed factors were used to try to clarify unusual high or low exposures.

3.6.2 Comparison of VITAE and chemical analysis

To compare exposure assessment by both methods selected parts of coveralls were analysed by VITAE and consecutively by chemical analysis, according to the scheme given in Appendix F.

In order to assess agreement and systematic differences between VITAE- and chemical analyses Bland and Altman (1986) suggested as a first step to plot the data of both methods. The next step would be plots of the differences between values ($b - a$) against the corresponding mean of the two values ($(a + b) / 2$). The measure of agreement is then the calculation of the range of the range within which most of the disagreement occurred ($\text{mean} \pm 2\text{SD}$), or the limits of agreement. A mean difference close to zero and a small interval within the limits of agreement would illustrate good agreement.

Another approach is to plot the percentages of differences against the mean. The percentage of differences is calculated according to

$\% D = |a-b| / ((a + b) / 2)$, where

$\%D$: percentage of difference

$|a-b|$: absolute difference between chemical and VITAE analysis

$(a+b)/2$: mean of chemical and VITAE analysis

For the plots all data (pilot study and main study) were used.

4. Results

4.1 Pilot study

Two painters participated in the pilot study. One painter only sprayed the closet with the pneumatic spray painting technique. The fluorescent tracer on his hands after spraying with the pneumatic spray painting technique could not be removed adequately. This worker could only perform one or two spray applications a day. The other painter sprayed the closet and the boards and doors with both the airless and the pneumatic spray painting technique. The pressure for the airless spray painting technique varied from 50 to 100 bar, while the pressure for the pneumatic spray painting technique varied from 2.5 to 3 bar. A summary of some variables obtained in the study are given in table 4.1.

Table 4.1 Summary of the observed variables in the pilot study

	Person 1		Person 2	
	airless	pneumatic	airless	pneumatic
# closets	6	2	--	5
# doors/board	1	1	--	--
Duration closet (min) AM \pm SD (range)	11 \pm 2.8 (8-15)	10 (8-12)	--	18.3 \pm 5.7 (12-23)
Duration doors/boards (min)	9	18	--	--
spray volume (AM) closet (l)	2	2	--	2 (one time 4 l)
spray volume doors/boards	4	4	--	--
# number of replicates				

The theoretical calculated concentration of Uvitex in the paint varied from 82 to 92 mg/l (calculated from amount of Uvitex in the thinner and from the dilution of paint with the thinner). The concentration of Uvitex in paint was chemically analysed to be 54-108.6 mg/l. The value 108.6 mg/l is an extreme, all other analysed concentrations varied between 54 and 84.1 mg/l, with a mean of 77 mg/l. Two spikes were taken. The recovery of the spikes was 100%. For both the pilot study and the main study it holds that the coverall parts were analysed within 10 days.

Two measurements of person two were not considered in the calculation of the mean exposure. In one case the images could not be analysed. In the other case 4 litres of paint were sprayed for closets, which resulted in a much higher exposure.

Since the objective of the pilot study was to compare dermal exposure resulting from two different techniques for the same conditions of use, e.g. spray volume the results of this person were not included in the data analysis.

The results are only used to give an indication of the exposure, therefore only arithmetic means and normal standard deviations are given. Due to the low number of measurements, the results of the dermal exposure are clustered for the two persons.

Since the coveralls seemed not to be contaminated after spraying the boards and the doors, no coveralls were analysed with VITAE after spraying these objects. The eye is more sensitive for the presence or absence of fluorescence, therefore quantification with VITAE was useless.

The results of the pilot study are given below. In the tables only the results of spraying the closet are given.

Table 4.2: Total exposure of hands and forearms by airless and pneumatic spray painting.

Technique	Exposure due to airless spray painting (μg)				Exposure due to pneumatic spray painting (μg)			
	n	mean	std.	range	n	mean	std.	range
hands total	6	54	28	9.6-92	5	2	1.5	0.3-3.3
forearms total	6	0.7	0.8	0-1.9	5	<0.001	<0.001	0-0.001
total (hands, forearm)	6	55	28	9.6-93	5	2	1.5	0.3-3.3

The area exposed above the 'LOD' ranged for the forearms from 0 to 1597 mm², while the area exposed for the hands varied from 267 to 34338 mm². The area exposed was highest during airless spray painting (forearms: 5-1597 mm²; mean 769 mm², hands: 7476-34338 mm²; mean: 21072 mm²). The observed exposed area may be below the real area exposed area due to the fact that some pixels might contain Uvitex OB below the LOD. The LOD is given in an amount per area exposed.

The total area of the hands is roughly 60000 mm² (analysed by VITAE), while the area of the forearms is around 15000 mm². The area of both hands and the forearms is therefore around 75000 mm². This means that about 35% of the area of the hands is exposed ($21072/60.000 * 100$), while about 5% of the area of the forearms is exposed ($769/15000 * 100$) after airless spray painting. For pneumatic spray painting these values are 3% ($1748/60.000 * 100$) and 0.02% ($4/15.000 * 100$) respectively.

The exposure on hands and forearms per unit of area exposed (dermal area dose) is given in table 4.3. For this purpose the total exposure is divided by the area exposed. This is performed to get an indication of the mean dermal area dose. This value is used for the comparison with EASE, which given an exposure in $\text{mg}/\text{cm}^2/\text{day}$.

Table 4.3: Exposure on hands and forearms per unit of area exposed by airless and pneumatic spray painting

Technique Part of the skin	Exposure per area exposed due to airless spray painting (ng/mm^2)				Exposure per area exposed due to pneumatic spray painting (ng/mm^2)			
	n	mean	std.	range	n	mean	std.	range
hands total	6	2.4	0.6	1.3-2.9	5	1.1	0.6	0.5-1.9
forearm total	6	0.7	0.6	0.2-1.6	5	0.0	0.1	0-0.1
total	6	2.4	0.6	1.3-2.9	5	1.1	0.6	0.5-1.9

In tables 4.4 and 4.5 the results for the coverall are given.

Table 4.4: Total exposure on the coverall (μg) by airless and pneumatic spray painting.

Technique	Exposure due to airless spray painting (μg)				Exposure due to pneumatic spray painting (μg)			
	n	mea n	std.	range	n	mean	std.	range
	3	727	256	446-950	3	72	32	45-108

The area exposed for the coverall ranges for the pneumatic spray painting technique between 864 and 2325 mm^2 (mean is 1487 mm^2), for the airless spray painting technique the area exposed ranges from 5821 to 9051 mm^2 , with a mean of 7898 mm^2 . The total area of the coverall is around 2400000 mm^2 . This means that after airless spray painting about 32% of the area of the coverall is exposed, for the pneumatic spray painting this is about 6%.

Table 4.5: Exposure per unit of area exposed (ng/mm²) on the coverall for airless and pneumatic spray painting

Tech- nique	Exposure per area exposed due to airless spray painting (ng/mm ²)				Exposure per area exposed due to pneumatic spray painting (ng/mm ²)			
	n	mean	std.	range	n	mean	std.	range
Part of the skin (coveral l)								
overall expo- sure (all skin sites)	3	0.9	0.2	0.8-1.1	3	0.5	0	0.5

Tables 4.2 through 4.5 contain the results of the spraying of the closet. The doors and the boards were only sprayed twice, one time with the airless spraying technique (total exposure hands and forearms is 6284 ng) and one time with the pneumatic spray painting technique (total exposure on hands and forearms is 3749 ng). No coveralls were analysed.

When the dermal exposure values of airless and pneumatic spraying are compared, it is obvious that the exposure is highest during airless spray painting (no statistical analysis was performed).

The above results emphasized the need to perform a more extensive study in which a larger object would be sprayed by the airless spray painting technique. It was expected that in such a study the exposure would be higher than what was observed in this study.

4.2 Results of the study during spray painting the containers

4.2.1 Descriptive statistics

Exposure was measured in three off-shore enterprises. In total 12 workers participated in the study. Measurements were performed while the in- or outside of a container was sprayed with the airless spraying technique. The outside of the container was painted 22 times, while the inside was painted 5 times (see Table 4.6). The mean duration of spraying, the mean spray volume, the diameter of the orifice of the nozzle which is used and the angle of the paint flow are given in Table 4.6.

Table 4.6 Summary of the observed variables in the three different enterprises

	Workplace A	Workplace B	Workplace C
# inside	1	2	2
# outside	8	8	6
Duration outside (min)	11.5 ± 5.2	9.8 ± 3.5	11.8 ± 4.1
AM ± SD (range)	(4 - 21)	(4 - 16)	(8 - 19)
spray volume (l)	7.0 ± 2.8	6.1 ± 1.6	6.5 ± 2.7
AM ± SD (range)	(3.1 - 12.8)	(3.4 - 8.5)	(3.0 - 9.5)
Orifice (µm)	130	254	330
Angle of paint flow (degrees)	30	40	65
#	numbers of spray paint activities		

The 90 percentile of the duration was about 16 minutes for spraying the outside of the container and 9 minutes for spraying the inside of the container. The coverall measurements of one person painting the outside of the container were excluded, since the recordings could not be analysed. No skin exposure measurements were excluded.

In appendix G more detailed information (in Dutch) is given about the position of the container in the workplace, the circumstances and the observed variables during each time the container was painted.

4.2.2 Quality control

On each day of sampling two spikes were taken to determine the stability of the substance during transport and storage. The recoveries varied for the high concentration from 100 to 110%, with a mean of 106%, and for the lower concentrations from 92 to 125%, with a mean of 108%.

On each day of sampling two field blanks for chemical analysis were taken, which resulted in a total of 12 blanks. Since on only a few blanks an amount of Uvitex OB was found, the exposure was not adjusted for the blanks. Next to the blanks for the chemical analysis, one blank coverall was used to measure the background of a Tyvek coverall by VITAE analysis. 38 VITAE images were taken from this coverall. On three of the coverall parts fluorescence was observed. The maximum amount found on a piece of the coverall was 2.6 ng. A total amount of 3.1 ng was found on the coverall.

In total 30 samples of paint were taken. The calculated concentration of Uvitex OB in paint was 66.7 mg/l (1.4 g Uvitex OB in 1 litre refined petrol, in 20 litre paint: $1.4 \text{ g} / 21 \text{ l} = 0.0667 \text{ g/l}$). The measured concentrations varied from 39.0 to 108.6 mg/l (mean: 64.8). If both the lowest and highest concentrations were left out, the

concentrations varied from 58.7 to 70.3 (mean: 64.2). The Uvitex OB concentration in paint measured by the chemical analysis are used in the statistical analysis procedure.

4.2.3 Statistical analysis

Statistical analysis showed that the data of the VITAE analysis did not follow a normal or a lognormal distribution. Therefore, both the AM and the GM are given in the tables. The statistical tests used are all non-parametric tests, except the test used to study the difference between spraying the container for the first and the second time (paired sample *t* test). The levels of exposure given in this chapter are the level of exposure to tracer (Uvitex OB).

Ten persons painted the outside of the container two times. Two persons sprayed the outside of the container one time. In the following it is tested whether the two spray applications can be considered as two independent observations by using the paired sample *t* test (two sided). A significant difference between the skin exposure (ng) after painting the outside for the first and the second time ($p < 0.03$) is observed. The exposure was higher after the first spray painting application. This difference is also present for the exposure on the Tyvek coverall ($p < 0.04$). The spray volume for spraying the container for the first and the second time are not significantly different ($p < 0.16$). There is also no significant difference between the duration of spray painting for the first and the second time ($p < 0.28$). It was decided, partly due to the low amount of measurements, to consider the first and the second spray painting application (spray painting the outside for the first and the second time) as two independent observations. The inside of the container was sprayed once by 5 spray painters.

In Table 4.7a the statistical distribution parameters (arithmetic mean, geometric mean, standard deviation, geometric standard deviation, range and 10th and the 90th percentile) of total coverall exposure and coverall exposure per area exposed after painting the in- or outside of the object, are given. The area exposed is the part of the VITAE image that is considered exposed by the VITAE system. The coverall exposure (μg) and the coverall exposure per area exposed (ng/mm^2) are both significantly higher after spray painting the inside of the container. The exposed area ranges from 175 to 4966 cm^2 with a mean of 2061 cm^2 for spraying the outside of the container and it ranges from 1571 to 8987 cm^2 with a mean of 6467 cm^2 for spraying the inside of the container. The area of the coverall is approximately 23.000 cm^2 . This means that up to 35% ($23.000/8987 \cdot 100$) of the total body area is exposed. In Table 4.7b the statistical distribution parameters of total dermal exposure and dermal exposure per area exposed of the skin, after painting the in- or outside of the object, are given. There is no significant difference between the skin exposure (μg) and the skin exposure per exposed area after painting the inside or the outside of the container. The total area exposed of the skin ranged from 0.07 to 176 cm^2 , with a mean of 73 cm^2 , for spraying the outside of the container, and it ranged from 17 to 154 cm^2 with a mean of 107 cm^2 after spraying the inside of the container. The area of the hands and the head is about 600 cm^2 (the

area of the head is about 100 cm²). This means that up to about 30% (107/600 * 100) of the hands is exposed. One person spraying the outside of the container had a high skin exposure, this was a person spraying with both hands. Contact with a contaminated spray gun could be the reason of this high exposure.

In the following statistical analysis, the results after painting the inside of the container are analysed separately from the results after painting the outside. Next to the above mentioned analysis, the following analyses were made: exposure on spray hand versus non spray hand and the exposure on the back and front of the coverall. The results of these analysis are given in appendix H (table 1 and 2).

In Table 4.8 the statistical distribution parameters of exposure (skin and coverall) for the three different companies are given. When the AM is considered it appears that workers in workplace C have the highest exposure (µg), however, when the GM is considered it appears that the workers in workplace B are highest exposed. This difference is caused by the fact that the variability in exposure between the workers in workplace C is very high. The difference in exposure between the companies is not significant. When the median of the total exposure is considered, company C has the highest exposure (A: 131 µg; B: 93 µg; C: 164 µg) When the median of the coverall exposure is considered company C has the highest exposure (A: 131 µg; B: 83 µg; C: 161 µg). When the median of the skin exposure is considered company B has the highest exposure (A: 0.6 µg; B: 7 µg; C 3 µg). The other results for the skin and the coverall are given in appendix I.

The distribution of the total exposure (skin and coverall) over several parts of the body is given in Table 4.9. It can be seen that the exposure is not distributed equally over the body. The lower legs have the highest exposure, regardless whether the in- or outside is painted (54% after spraying the outside of the container, 48% after spraying the inside of the container; the area of the lower legs is about 12% of the total area). The percentage of the area exposed as detected by VITAE, related to the total area of the coverall and the skin is given in appendix H. The lower legs (for the coverall), and the hands (for the skin) have the highest percentage of the area exposed, regardless whether the in- or outside is painted.

The exposure is also calculated per amount of Uvitex used. An average potential exposure of 746 mg/kg Uvitex OB (range 12 - 5801 mg/kg) was calculated for airless spray painting (n=26). The mean potential exposure after painting the inside of the container is 2280 mg/kg tracer (range 613 - 5801, n=5), while the mean potential exposure is 398 mg/kg tracer after painting the outside of the container (range 12 - 1896, n=21).

Table 4.8 Statistical distribution parameters of coverall and skin exposure and coverall and skin exposure per area exposed during painting the outside of the container, given for the different workplaces

	n	Exposure					Exposure per area exposed						
		AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Workplace A	8	154	156	83	3.8	11 - 472	21 - 303	0.7	0.2	0.7	1.4	0.4 - 1.0	0.5 - 1.0
Workplace B	7	125	80	107	1.8	47 - 290	67 - 207	0.6	0.2	0.6	1.4	0.3 - 0.8	0.4 - 0.8
Workplace C	6	179	168	71	7.6	2.2 - 449	10 - 361	0.6	0.3	0.5	2.1	0.1 - 1.0	0.3 - 1.0

AM: Arithmetic Mean
SD: Standard Deviation
GM: Geometric Mean
GSD: Geometric Standard deviation
10th-90th perc.: 10 to 90 percentile

Table 4.9 Distribution of total (potential) dermal exposure over the body in percentages, after painting the in- or outside of the container.

	Percentage of total exposure (%)					
	Outside (n=21)			Inside (n=5)		
	AM	SD	Range	AM	SD	Range
Lower legs	54	30	13 - 97	48	25	33 - 93
Upper legs	18	19	0.1 - 66	17	12	1.4 - 28
Torso	13	11	0.4 - 31	17	10	0.2 - 26
Forearms	7.3	8.8	0.0 - 34	7.6	4.1	0.8 - 11
Upper arms	2.0	2.4	0.0 - 7.9	4.2	2.3	0.5 - 6.6
Hands	3.6	4.8	0.0 - 16	2.1	1.9	0.5 - 4.3
Head*	2.3	2.9	0.01 - 10	3.2	2.4	0.05 - 6.4

*: Both hood of the coverall and face.

Table 4.10: Percentage of the area exposed (skin), related to the total area, given for several parts of the body, after painting the in- or outside of the container

	Percentage of the area exposed (%)					
	Outside (n=22)			Inside (n=5)		
	AM	SD	Range	AM	SD	Range
Hands	9.5	12	(0.0 - 41)	17	11	(4.0 - 32)
Head	1.1	3.1	(0.0 - 15)	1.5	2.4	(0.0 - 5.6)

The 10 to 90 percentile for the percentage of the exposed area varies for the hands after spraying the outside of the container from 0.06 to 26%, the same range varies from 7.3 to 27% after spraying the inside of the container. The contribution of the exposure of the head is limited, therefore also exposure values for solely the hands are given (Annex H; table 5).

The dermal area dose for the total skin and coverall area is given in appendix H table 6.

4.3 Linear regression analysis

The spray volume (l) and the duration of painting (min) were examined as potential exposure determinants. They were only analysed for painting the outside of the container, because the inside was painted only five times. The analyses were done separately for skin and coverall exposure (ng). There was no significant relation between the spray volume and the skin exposure ($R^2 = 0.03$, $p = 0.21$), nor between the spray volume and the coverall exposure of the coverall ($R^2 = 0.04$, $p = 0.20$). The duration of painting also had no relation with exposure of the skin ($R^2 = 0.05$, $p = 0.97$), nor with exposure of the coverall ($R^2 = 0.03$, $p = 0.21$). However, person 8 appeared to be an outlier. Person 8 sprayed more paint, and therefore achieved a thicker lacquer layer than the other painters.

Excluding person 8 resulted in a significant relation between exposure on the coverall and duration ($R^2 = 0.21$; $p = 0.025$ for duration) and the spray volume ($R^2 = 0.26$; $p = 0.012$). Excluding person 8 resulted for the skin exposure only in a significant relation between exposure and volume of paint sprayed ($R^2 = 0.15$; $p = 0.046$), no relation between duration of spray painting and exposure ($R^2 = 0.05$; $p = 0.78$) was found. Since spraying and duration were correlated ($R^2 = 0.61$, $p < 0.01$) no multiple regression was performed.

In the exposure assessment, exposure will be extrapolated with duration, therefore, only the equation derived for exposure and duration of spray painting is given below:

$$E = 17820 t - 31573$$

in which:

E = Exposure (ng)

t = duration of painting (min).

Since duration of exposure explains only 21% of the variation in the exposure, the derived exposure by this formula is only indicative.

The used pressure could not be measured during painting, so the correlation between exposure and pressure was not studied.

4.4 VITAE analysis versus chemical analysis

Appendix E (figures E 2 through EA) shows the plots of comparison the two methods for exposure assessment of 43 coverall parts. Especially for the lower exposed coverall parts, the percentage of difference of both methods is high (figure E3). No difference could be observed for the results of the pilot study and the main study. Figure E4 illustrates the wide range of the limits of agreement (mean of differences $\pm 2SD$) indicating poor agreement between both methods. However, the mean of differences is close to zero, which indicates no systematic over- or underestimation by one of the methods over the observed range of exposures.

5. Discussion

5.1 Introduction

There are several direct and indirect techniques to assess occupational dermal exposure. The advantage of a tracer technique above other techniques is that it is a direct technique for quantification of dermal exposure to chemicals. The high sensitivity of the system allows the detection of even minor incidents of dermal exposure (Fenske *et al.*, 1986). In addition the technique gives an indication of the exposed area. Before the study will be discussed thoroughly, the validity of values derived by the VITAE system will be discussed.

5.2 Validity of the VITAE analysis

The range of quantification of Uvitex OB on a Tyvek coverall lies approximately between 30 and 250 ng/cm² (grey value of the pixel from 1 to 60). In view of tests performed previously to the study, it was expected that most exposure could be quantified accurately. The tests showed that the resulting exposure by spray painting would be within the range of quantification. Only high exposures might be under-estimated, due to the exclusion of overexposed parts of the coverall (>250 ng/cm²).

However, regarding the comparison of the VITAE with the chemical analysis this appears not to be true. Especially at the images containing over-exposed parts, VITAE gives a higher exposure compared to the chemical analysis, whereas at the other images, the system generally under-estimates the exposure. What process causes the overestimation is not clear. The over-exposed coverall parts are, however, expected not to have a large influence on the total exposures found in this study. From the 1080 VITAE images analysed in this study, only twenty (less than 2%) had over-exposed parts in it. The overexposed parts were distributed over different coverall parts of several workers.

The under-estimation of the exposure by VITAE might be due to the fact that it was not possible to determine a LOD in the 'classical way', as it is performed with the chemical analysis by taking three times the standard deviation of a series of blanks. The LOD for VITAE must be determined per pixel. It was tried to derive a LOD by using the coverall parts which were analysed both chemically and by VITAE. This procedure is given in appendix J. Including a LOD on the non-detectable pixels of the coverall, as described in appendix J, resulted in a new exposure range which increased only slightly. The influence was highest where the exposed area is the smallest. The upper limit of the exposure increased with 16% (spraying inside of the container) and 33% (spraying outside of the container). These results only hold for coverall exposure. The results found in the study are therefore not adjusted by including a LOD.

An increase in the used tracer may result in an increase in both the dermal area dose and the exposed area. Spray painting is assumed to cause a more or less

homogeneous distribution of the exposure over the body. Fenske and Birnbaum (1997) distinguished in a recent study 4 sorts of exposure: 1: no exposure; 2: high exposure; 3: intense exposure (high intensity spatially limited); and 4: diffuse exposure (spatially extensive; low intensity). The authors stated that intense exposure might result from spray droplet deposition, splashing or holes in protective clothing. Diffuse exposure might result from contact with fine sprays or contaminated surfaces. The exposure pattern due to airless spray painting may be a combination between the diffuse and the intense exposure pattern. This means exposure over the complete area of the coverall and skin with some intense spots.

It is not certain whether VITAE gives an underestimation of the exposure of the skin, since no chemical analysis was performed on the skin exposure.

In the following the results of the pilot study and the main study are compared and discussed.

5.3 Comparison of the measured values in the main study with the pilot study

From the study it appeared that the dermal exposure in the pilot study is higher than in the main study. The mean skin exposure (hands and forearms) during spraying the closet with the airless spray painting technique, was 55 µg, against a mean exposure of 7 µg during spraying the outside of the container, and a mean exposure of 11 µg during spraying the inside of the container (all tracer). The mean coverall exposure during spraying the closet with the airless spray painting technique was 727 µg, while mean coverall exposures of 144 and 558 µg were measured during painting the outside and the inside of the container. The dermal exposure was less when the closet was painted with the pneumatic spray painting technique (mean exposure of 2 µg on the skin and 72 µg on the coverall). The exposure in the pilot study was higher despite the fact that the spray volume and the duration of spray painting in the pilot study was less (about 2 litre; with a duration between 8 and 15 minutes) than in the study painting the containers (the spray volume varied from 3 to 13 l per application; with a duration between 4 and 21 minutes). The concentration of Uvitex OB in paint was similar.

Data on dermal exposure from the pilot study revealed a higher exposure resulting from airless spraying compared to pneumatic spraying. According to the higher deposition efficiency of higher airless spraying and a resulting lower overspray (see 2.2) an inversed result was expected. However, the reported general deposition efficiency for this technique may be an overestimation for this specific (non-flat, relatively small) object. In addition, the gun-to-object distance (<0.5 m) is small compared to the gun-to-object distance for large flat objects which. In the main study this distance was on average 1m. These factors may affect deposition efficiency and overspray very much and thus the degree of exposure.

The difference in exposure between the pilot and the main study may be caused by the fact that due to the available space during spraying the inside of the closet, the

mist of the paint is much closer to the painter when a closet is painted (a special shaped object with much corners) than when a container is painted (spraying the outside is a flat object). Furthermore there is a difference in distance when the closet or the container is sprayed. The distance between the painter and the object is less when the closet is painted. (painters stay almost inside the closet, which is approximately 2 m (in height)). These results suggest that the situation studied during spraying the containers may not be a reasonable worst case situation, unless it is very unusual to spray a object like a closet, in which the painter is very close to the object, with an airless spraying technique.

In the following the results of the study during spraying the containers will be discussed more thoroughly.

5.4 Main study

Ten persons painted the outside of the container two times. The exposure was significantly less when the container was painted for the second time. This might be due to the fact that the spraying was performed less accurate when the container was sprayed for the second time. It might also be due to habituation or because it was more difficult to see which part of the container was wet and which part was not when the container was sprayed for the second time. When the Spearman rank test is performed on these data, it appeared that there is a statistical significant relation between the first and the second spray painting application ($p < 0.05$; $r_s = 0.92$). This means that when person one had the highest exposure after the first application, the exposure of person one was also highest after the second application.

The inside of the container was sprayed by 5 persons. The (potential) dermal exposure during spraying the inside of the container is higher than during spraying the outside. This may be due to the fact that a higher percentage of the overspray is available for deposition and back bouncing from more sides is likely to occur when the inside of the container is sprayed.

In the present study, it was attempted to keep the working conditions similar for the different painters by taking one object to be painted, one spray painting technique and one sort of paint (semi-experimental set-up). In spite of this, dermal exposure showed a large variability (range 2 - 814 μg). Regression analysis was done to study whether duration of painting and spray volume showed any influence. After excluding the exposure of one person (person 8), both factors appeared to be significantly related to the coverall exposure. For skin exposure, only the spray volume showed to be an exposure modifier, duration was not. Up to 26% of the variation in the coverall exposure could be explained by the spray volume; up to 21% could be explained by duration. Since the two variables are highly correlated, the combined influence will be less than the addition of 26 and 20%. Next to duration and spray volume, there will be other factors which cause the high variation in exposure. Several individual variables were registered, such as

the hand used to paint, the way of painting and the distance between the painter and the container. None of them could be identified as exposure modifiers by linear regression.

The study confirms that the substance is not distributed equally over the body. Fenske *et al.* (1986) mentioned that dermal exposure is often episodic and unpredictable in nature (*e.g.* spills or splashes), making many systematic sampling procedures impractical. The patch technique, for example assumes that exposure is uniform over an entire body region, whereas deposition patterns do not appear to be uniform based on fluorescent tracer evaluation. With chemical analysis it is also generally assumed that the analysed area is exposed totally and homogeneously. With the VITAE technique it is possible to study whether the distribution over a certain body region is uniform. For this study it appeared that the distribution over the body is not uniform. Up to 40% of the area of the coverall is exposed after spraying the inside of the container, for the hands this percentage is up to 32%. After spraying the outside of the container the percentages are for the coverall and the hands 22% and 41% respectively.

The distribution of the contamination over the body parts shows that the lower legs have (percentage wise) the highest exposure (Table 4.9). Painting the top of the container and more back bouncing by spraying the lower part or the sides of the container may account for this effect. Notable is that the distribution over the body is nearly almost similar after painting the in- or outside of the container. Brouwer *et al.* (1997) studied the distribution of the pesticide propoxur over the body after spray application in glasshouses for carnations. The highest amount was found on the lower legs of the spray operators (approximately 45%), approximately 18% was found on the upper legs. The lowest amount was found on the head (approximately 0,2%). De Vreede *et al.* (1994) studied the distribution of methomyl, a pesticide, over the body after high-volume spray application in greenhouses for chrysanthemum. The highest amount was found on the hands of the workers (37%). On the upper legs 22% was found, while 14 % was found on the lower legs. The head was left out of consideration in this study. In comparison with the results from studies on pesticides a very low percentage of the total exposure was found on the hands of the spray painters (ca. 4% after painting the outside, ca. 2% after painting the inside). In the study described by Brouwer *et al.* (1998) and de Vreede *et al.* (1994) 15% and 37% respectively was found on the hands. No clear explanation can be given for this difference. It must be taken into account that there are considerable differences between spray painting and spray application of pesticides. In spray painting a spray is directed specifically at a flat, nonflexible surface, whereas pesticides are sprayed more dispersely on a surface of leaves. Therefore both the pattern of back bouncing and the intensity may deviate considerable from spraying pesticides.

The possibility to determine a dermal area dose (D_A) may be important in view of risk assessment. When it is assumed that the substance is distributed equally over the exposed surface, a lower D_A is calculated compared to some local D_A values calculated with use of the VITAE analysis (exposed surface area < total analysed

surface area). For a given exposure dose the D_A may increase if the exposed area becomes smaller, and thus the absorption percentage will stay equal or will decrease when the maximum flux is reached (Bos et al., 1998).

5.5 Comparison with exposure models

When EASE is used to estimate dermal exposure due to spray painting activities, it is assumed that mainly the hands will be exposed. A spray painting application is estimated by EASE as 0.5-1.5 mg/cm²/day, assuming a wide-dispersive use scenario with direct contact, an extensive contact level and a concentration of a non-volatile substance in paint of 10%.

When a homogeneously exposed area of the hands of 600 cm² (exposed area of the hands derived from VITAE) is assumed, the exposure is estimated to vary from 300 to 900 mg/day (600*0.5; 600*1.5). In this estimate it is assumed that the activity is performed for about 3 hours per day. In a normal estimate, the exposed area of the hands is assumed to be 840 cm². The observed exposed area is less due to the fact that the sides of the fingers and the hands are not considered in VITAE and the wrist is not included.

To be able to compare the exposure values with the estimates made by EASE, the measured dermal exposure values must be adjusted to a certain non-volatile compound in paint. This is only possible when it is assumed that Uvitex OB behaves like a non-volatile compound in paint: the vapour pressure of Uvitex OB is very low (2.5×10^{-8} Pa at 20°C) and the Uvitex OB is assumed to be dissolved in the paint completely and homogeneously.

The mass percentage of Uvitex OB in the paint was 0.0074%. When a mass percentage of a non-volatile compound in paint is assumed to be up to 10%, the measured amounts of Uvitex OB (Table 4.7) must be multiplied by $10/0.0074=1351$. In the exposure models only exposure to the hands and the face is estimated, therefore, only the skin exposures found in this study will be translated into a 10% a non-volatile substance concentration.

The skin exposure for a non-volatile compound in paint, with a concentration of 10%, is therefore calculated as follows:

- skin exposure (face, hands), after painting inside: 2 - 42 mg;
10-90 percentile: 5 - 30 mg;
- skin exposure (face, hands), after painting outside: <0.02 - 70 mg;
10-90 percentile: <0.02 - 27 mg.

The highest skin exposure (70 mg) was found for a person spraying the outside of the container, both right- and left handed. The mean skin exposure, assuming a non-volatile substance concentration of 10%, is calculated as 10 (spraying outside of the container) and 14 mg (spraying the inside of the container). Considering the exposure on the coverall, the exposure is calculated as 3-1090 mg with a mean of 400 (spraying inside of container) and 170 mg (spraying outside of the container).

Comparing the exposure estimated by EASE (300-900 mg/day) with the skin exposure derived from the study, it appears that EASE overestimates the exposure extremely.

However, some remarks have to be made regarding this comparison. EASE estimates a daily exposure, whereas the duration of the spraying of the container varied from 4 to 21 minutes with a mean of about 10 minutes and a 90 percentile of 16 minutes. It is assumed that during a full shift working day, the total duration of spraying activities may be at least 3 hours. It is likely that the exposure measured in the study would be higher when 3 hours of spray painting were considered. Although there is no clear relation between skin exposure and duration of spray painting, the skin exposure will be extrapolated to a 3 hour exposure by proportional extrapolation. When the extrapolation to a 3 hour period (180) of exposure is made, considering the highest 90 percentile exposure after 10 min of spraying and a non-volatile substance concentration of 10% (30 mg), the skin exposure is calculated as 540 mg $((180/10)*30)$.

The dermal area dose on the skin (hands and face) found in this study varied from 0.1 to 2.9 ng/cm² after spraying the in- or outside of the container. The highest 90 percentile dermal area dose was 1.9 ng/mm².

When it is assumed that the dermal area dose on the skin increases proportional with the substance concentration in paint, the 90 percentile dermal area dose, considering a non-volatile substance concentration in paint of 10%, is calculated to be 2566 ng/mm² (≈ 0.3 mg/cm²; $1.9*1351$). This dermal area dose holds for the exposed area. Up to 40% of the hands is exposed with a 90 percentile value of 27%.

The calculated 90 percentile exposures and the exposure estimated by EASE is given in table 5.1

Table 5.1: The calculated exposure derived from the 90 percentile values of the study against the estimates made by EASE.

	Study results*	EASE estimate
exposure (mg)**	540	300-900
dermal area dose (mg/cm ²)***	0.3	0.5-1.5
percentage of area exposed	27	100

*: based on highest 90 percentile values of the study (exposure extrapolated to both 3 hour of exposure and a substance concentration of 10%)

** : based on a non-volatile substance concentration of 10%, an exposure duration of 3 hours and an exposed area of 600 cm²

***: the dermal area dose for the exposed parts of the skin; based on a non-volatile substance concentration of 10%.

The (90-percentile)dermal area dose for the exposed skin area agrees reasonable well with the estimate made by EASE. Considering the extrapolated exposure levels it is concluded that there are indications that the EASE estimate agree reasonably well with the measured levels of exposure. However, this can only be seen as a preliminary, indicative, conclusion because of the uncertainties in the extrapolations and the measurement method. A proportional increase of exposure due to increase of the non-volatile substance concentration in paint and duration of exposure is assumed. This might result in an overestimation of the exposure. On the other hand, due to the (possible) presence of tracer on the non-detected parts of the coverall (LOD), the real exposure might be higher than the measured exposure. More information is necessary to fully verify the true exposure. This information should preferable come from studies with higher concentrations of the measured substance in the paint and longer period of exposure.

In addition, the comparison of EASE with the measured exposure levels is only applicable for the non-covered part of the body. Since approximately 95% of the exposure is present on the coverall, it is likely that either by penetration through the coverall, through leakages, other parts of the skin surfaces will be exposed. The forearms might be exposed due to this process and via not tight-fitting sleeves. Since the coveralls worn in the present study had an elastic band on the sleeves, leakage via the sleeves is considered to be low.

6. Conclusions and recommendations

In this final chapter the questions raised in the introduction will be considered and recommendations for further studies will be given.

6.1 Conclusions

The results show deposition of the paint spray due to airless spray painting. In spite of the semi-experimental setting of the study (one object, one spray painting technique) the variation in the potential dermal exposure is notable (ranging from 2 to 806 μg and from <0.01 to 52 μg tracer on the coverall and skin respectively). The exposure after painting the inside of the container is significantly higher than after painting the outside of the container.

When the exposures of the coveralls derived by chemical and VITAE analysis were compared, it appeared that the chemical analysis gives generally higher exposures than the VITAE analysis. This might be caused by the absence of a valid LOD on the non-detectable pixels. Incorporating an estimate of a LOD did, however, not influence the exposure much.

The VITAE technique shows that some body regions are higher exposed than others. 54% of the exposure was present on the lower legs (being about 12% of the total area) after spraying the outside of the container, 48% of the exposure was present on the lower legs after spraying the inside of the container. Compared to studies of hand-held spraying of pesticides in glasshouses, the contribution of exposure of the hands of the painters to the total body exposure is relatively low (ca. 3% versus 15% and 37%).

It furthermore appears that most non-volatile compounds deposit on a rather small percentage of the total body area. Up to 40% of the area of the hands is exposed, with a mean of 12% for spraying the outside of the container and a mean of 11% for spraying the inside of the container. Also up to 40% of the area of the coverall is exposed, with a mean of 7% after spraying the outside of the container and a mean of 13% after spraying the inside of the container.

The following skin exposure values are derived from the study. When a concentration of a non-volatile substance in paint of 10%, and an exposure duration of three hours is assumed, the exposure to the hands is calculated to be up to 540 mg (based on the highest 90 percentile exposure and duration), whereas EASE estimates an exposure of 300-900 mg/day. It has to be considered that for all extrapolations proportional linearity is assumed, this may give an overestimation of the exposure.

The dermal area dose found in the study is near the lower limit of the range of the estimate made by EASE. In this estimation a non-volatile substance concentration

of 10% in paint is assumed. Assuming a homogeneous distribution over the body and a concentration of a non-volatile substance in paint of 10%, the dermal area dose in the study was estimated to be 0.3 mg/cm² on the skin (based on the highest 90 percentile dermal area dose of the skin). EASE estimates a dermal area dose which varies from 0.5-1.5 mg/cm²/day. Considering that the results from the study hold for a mean exposure duration of 10 minutes, the daily dermal area dose will probably be somewhat higher. For the dermal area dose no extrapolation to a 3 hours exposure was made. It is believed that increase in exposure is assumed to be caused by increase of both the area exposed and the dermal area dose.

Considering that 95% of the exposure during spray painting occurs on the coverall, it is likely that not only the hands and the face are exposed. Other parts of the skin might also be exposed due to penetration through the clothing. Especially the forearms might be exposed due to this process and due to leakage via not tight fitting sleeves.

The above mentioned results suggest that the exposure estimates by EASE of the present exposure scenario agrees reasonable well with the exposure measured in the study, and exposure estimates do not need to be adjusted. However, there are many uncertainties, especially regarding extrapolation to duration and concentration of the substance in paint. Therefore, additional studies are needed, especially studies aimed at a higher tracer concentration and a longer exposure duration, to enable a more thoroughly discussion on exposure estimates by EASE.

6.2 Recommendations

The study reported here is only a small scale study of a single type of spray painting (airless) with a tracer. More field studies are needed for range finding of exposure due to the use of other spraying techniques, so the performance of exposure estimates by EASE can be evaluated over a wide range of exposure situations.

It seems that the personal work-method of the workers is of importance for the dermal exposure to paint due to airless spray painting. It is recommended to pay more attention to the individual work-method, in order to study the influence of these factors on dermal exposure. To be able to distinguish exposure modifiers it is recommendable to keep most factors stable (*e.g.* room in which is painted, painter, object) while one possible modifier will vary at a time (*e.g.* duration of spray painting).

Future study should be aimed at more and longer duration spray applications. Preferably these study should be done with higher concentrations of measured substance in the paint, which will facilitate the extrapolation of the exposure to a higher non-volatile substance concentration in paint

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8. Signature

A handwritten signature in black ink, consisting of several loops and a long, sweeping tail that extends to the right. The signature is positioned above a horizontal line.

J.J. van Hemmen
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Appendix A Ease dermal exposure model

Introduction

The EASE model, dermal exposure part, developed by the U.K. Health and Safety Executive, can partly be seen as an extension of the ad hoc analogy approach. The U.K. HSE has modified the model of U.S. EPA, that is supported by empirical studies with liquids, to include the effect of multiple contacts.

Model

From the U.K. National Exposure Data Base and studies and ideas reported by the U.S. Environmental Protection Agency (EPA) data for combinations of substances and situations, assigned to categories for the same aspects, have been studied by experts from the HSE. These experts have derived generic exposure values for relevant combinations of these aspects.

The number of contacts of the skin with the contaminant is an important parameter in the assessment of skin exposure. For the assessment of skin exposure to solid substances no theoretical or empirical supporting data is provided.

Table 2.1 is derived for assessment of potential skin exposure.

Table 2.1 Determination of skin exposure

Physical state	Pattern of use	Pattern of control	Contact level (mg/cm ² /day)			
			None	Incidental	Intermittent	Extensive
gas, vapour or not dusty solid			very low	very low	very low	very low
liquid, aerosol (solid or liquid) or solid	closed system		very low	very low	very low	very low
	inclusion on to matrix or non-dispersive use	not direct handling	very low	very low	very low	very low
		direct handling	very low	0 - 0.1	0.1 - 1	1 - 5
	wide dispersive use	not direct handling	very low	very low	very low	very low
direct handling		very low	0.1 - 1	1 - 5	5 - 15	

References

TGD. Technical Guidance Documents in support of the Commission Directive 93/67/EEC on risk assessment for New Notified Substances and the Commission Regulation (EC) 1488/94 on risk assessment for Existing Chemicals. European Chemicals Bureau (Ispra) 1996.

Appendix B Spray painting techniques

Pneumatic spray painting techniques

The compressed air or pneumatic spray painting technique is most widely used because of its versatility and because it creates a high quality finish. In pneumatic (or conventional) spray painting guns, compressed air (with a pressure of 4 to 6 bar) is accelerated through a nozzle where a reduction in static pressure occurs. The reduced static pressure causes the paint to flow from a cup into an orifice where the atomization occurs. When this cup is below the nozzle the gun is called 'siphon cup' or 'suction' spray painting gun. When the cup is above the nozzle, the flow of paint is augmented by gravity and such guns are called 'gravity feed' spray guns (Heitbrink *et al.*, 1994). Around the paint flow there is a circular airstream with high velocity which disperses the paint. As a result of the surface tension, the paint particles form round bullets, which are swung away from the dispersion point. The paint particles may reach a maximum velocity of about 30 m/s. The mean diameter of the paint particles which are dispersed with pneumatic spray painting is between 40 and 80 micrometer (Doorgeest *et al.*, 1986; Kettenis *et al.*, 1991).

Two types of nozzles are used to disperse the paint: external mix and internal mix nozzles. In the external mix nozzle, the paint and the compressed air exit from separate orifices and are mixed outside the nozzle. Internal mix nozzles combine the compressed air and paint inside the nozzle (O'Brien and Hurley, 1981).

The advantages of the pneumatic spray painting technique are:

- equally painted surfaces can be achieved;
- relatively easy and largely applicable;
- it is applicable for porous surfaces;
- spraying of complex objects is possible.

Disadvantages of this technique are:

- next to the spray gun other equipment is necessary;
- to spray adequately, the sprayer has to be an expert.

(Kettenis *et al.*, 1991)

Airless spray painting techniques

The application of airless spray painting (hydraulic spray painting) does not demand compressed air to disperse and transport the paint. The paint is dispersed by forcing it through a nozzle with a very small orifice using high pressure. To get a smooth paint flow, the orifice of the nozzle is like a cleft. The airless spray painting gun consists simply of a device to hold the orifice and a valve for shutting off the flow. The hydraulic pressure necessary for atomization is provided by a high pressure pump with a maximum pressure of 600 bar (O'Brien and Hurley, 1981; Kettenis *et al.*, 1991). The dispersion of the paint will be determined by the viscos-

Appendix B

ity, the density and the surface tension of the paint, the size of the orifice and the velocity of the paint in the nozzle. The mean diameter of the paint particles formed with airless spray painting is larger than with pneumatic spray painting (Doorgeest *et al.*, 1986; Kettenis *et al.*, 1991).

The advantages of the airless spray painting technique are:

- a high mass transfer rate resulting in:
a thick lacquer layer achieved in one application and
a high pace of work;
- to spray adequately, the sprayer doesn't have to be an expert;
- it is applicable for porous surfaces;
- equal thickness of the lacquer layer on profiles can be achieved;
- relative little haze.

Disadvantages of this technique are:

- next to the spray gun other equipment is necessary;
- it is impossible to regulate the spray volume during spraying;
- limited spray pattern (problems with overlap);
- the choice of the nozzle depends on the paint and the application;

(Kettenis *et al.*, 1991)

Combinations of the pneumatic and the airless spray painting method also exist (airmix). An airless atomizer is used with an extra pneumatic air-current. The spray is generated in the same way as with the airless spray painting technique. With this technique, the hydraulic pressure is 10-60 bar, while there is a pneumatic pressure of 1-2 bar. The advantages of this method compared to the airless spray painting method are a spray pattern which is less limited and a larger dispersion of the paint particles. Compared to the pneumatic spray painting method there is less haze. Next to the spray gun, a high pressure pump and compressed air are necessary (Kettenis *et al.*, 1991).

Electrostatic spray painting techniques

With electrostatic spray painting, a negative electrical charge is applied to the paint particles during or after the dispersion of the particles. The negative charged particles follow the line of force of the electrostatic field between the electrode in the spray gun and the grounded object that has to be painted. In some automatic painting, the objects to be painted are charged. The dispersion can be achieved by use of pneumatic or airless equipment, or solely by use of electrostatic means. By use of electrostatic means only, the paint is being dispersed and transported electrostatically. The paint is introduced at the centre of a highly charged spinning disk. When the paint reaches the edge of the disk, the repulsive forces of the charges cause the paint to disperse. By use of pneumatic or airless equipment, only the transport of the particles is electrostatic. The electrical charge is applied to the particles, either by creating an ionized zone within the spray-cone area, or by imparting a charge to the fluid stream prior to its release from the spray gun (O'Brien and Hurley, 1981; Browne, 1983; Kettenis *et al.*, 1991). This technique can also be used for painting with powders (Heesen and van Raalte, 1994).

The advantages of this spraying technique, compared with pneumatic and airless spray painting, are:

- high profit;
- less haze;
- a better lacquer layer;
- less environmental pollution.

Disadvantages of this spraying technique are:

- it can't be used for each paint or lacquer;
- the equipment is less simple to handle;
- the initial expense is higher;
- a lower pace of work;
- sensitive for relative humidity.

(Kettenis *et al.*, 1991)

Heated paint can be used for any of the above described spray painting techniques. Heating the paint lowers the viscosity, which reduces the amount of solvent required. The lacquer layer cools rapidly after it is sprayed, which creates an applied coat that is much more viscous than a coat that is sprayed unheated. Painting can be applied at lower pressures, which reduces the amount of haze generated (O'Brien and Hurley, 1981; Heesen and van Raalte, 1994).

Appendix C Dermal exposure measurement techniques

Direct measurement techniques

Surrogate skin techniques

A collection of sampling devices attached to the worker or the worker's clothing is available. The most common is the use of an 'exposure pad' (Van Hemmen and Brouwer, 1995), consisting of several layers of surgical gauze and a cellulose paper backing. The gauze collects the solid contaminant, while the paper absorbs any liquid that may be deposited on the pad during exposure. The exposure pad is attached to the part of the body to be monitored and after exposure the gauze and paper are chemically analysed for presence of the contaminant(s). A major limitation in the interpretation of data from this method is the extrapolation from the small sample area represented by the pad to the entire area of the exposed skin. This can be overcome by using sampling devices which cover larger parts of the skin *e.g.* gloves or even coveralls. The estimated exposure using these sampling devices may be inaccurate due to differences in absorption or desorption characteristics between used device and skin, or differences in stability on the skin and on a sampling device (Van Hemmen and Brouwer, 1995).

Removal techniques

The exposure can be estimated by removing the contaminant from the skin surface by using wiping or washing the worker's skin and quantifying the amount of contaminant(s) on the swab or in the liquid used. Skin wipes or solvent rinses may not collect all of the contaminant deposited on the worker's skin during exposure. The mass of material that has penetrated into the epidermis during exposure may not be recovered and the quantity of contaminant remaining on the skin is excluded from the exposure estimates. This means underestimation of the actual dermal exposure (Van Hemmen and Brouwer, 1995). Appropriate laboratory removal efficiency studies are required as a part of quality assurance (McArthur, 1992; Fenske, 1993). The wipe technique proves to be unsatisfactory for the removal of materials from between fingers and around the finger nails (Durham and Wolfe, 1962), while the use of a solvent to wash the skin may alter the dermal absorption (Thomas, 1986).

Use of tracers

The use of tracers to mimic the actual contaminant of interest is a widely used technique in the field of chemical research. Possible tracers are pigments, fluorescent substances and to a less extent radioactive labels and neutron-activated substances (Van Hemmen and Brouwer, 1995). The use of a compound which emits fluorescent light instead of light of a visible wavelength has the advantage that workers get exposed without being aware of the exposure, so they are not

Appendix C

inclined to change their working habits. Another appealing advantage of the fluorescent tracer is the possibility to visualize the actual exposure using ultraviolet light. The visualisation has great importance for education and training purposes. These fluorescent tracer techniques have been adapted for assessing the quantity of material deposited onto the skin during labour. Shuresco (1980) and Vo-Dinh (1987) designed a portable optical spotter, which both induced and detected fluorescence, to evaluate deposition of contaminants itself onto the surface of the skin. In several studies the fluorescent tracer technique was used to assess the dermal exposure of workers to pesticides (Staniland, 1959; Franklin *et al.*, 1981). Fenske *et al.* (1986) were the first to report of a fluorescent tracer (in combination with an image analysis system) to investigate the dermal exposure of workers to pesticides quantitatively. Roff (1994) proposed a major advance in the illumination system used for quantifying fluorescence. His dodecahedral lighting system illuminates all skin surfaces evenly, reducing the number of correction factors which must be employed in the quantification procedures. Bierman *et al.* (1995) applied the fluorescent tracer technique in a field study to estimate the dermal exposure of spray operators and re-entry workers at five glasshouses for carnations, while also chemical analysis of clothing exposure was performed. The quantitative results of both techniques were compared. It was concluded that the variability in the fluorescent tracer technique was insignificant with respect to the variability in exposure within and between workers. The need to introduce a chemical substance (tracer) into the production process represents an important limitation of this approach (Fenske, 1993). The fluorescent tracer has to be used in such a way that it is relevant for the actual worker exposure. The tracer method is valid if the tracer and contaminant do not separate or act independently when a mixture is applied (Bierman *et al.*, 1995).

Indirect measurement techniques

Biological monitoring

The direct methods all estimate the amount of contaminant which has been deposited onto the surface, but do not indicate the amount of contaminant actually absorbed through the skin. Biological monitoring resolves this problem through analysis and quantification of the contaminant or its metabolite in blood, urine or expired air. The amount determined represents the exposure from all routes of entry. The dermal exposure can be calculated if the contribution to the total exposure by other routes is known. The use of the biological monitoring as a dermal exposure estimating technique necessitates data on the pharmacokinetics and -dynamics for each contaminant (Van Hemmen and Brouwer, 1995).

Surface sampling

To fully assess the potential hazards associated with exposures to contaminated surfaces, the mass of contaminant on the surface that may be transferred to the worker's skin must be determined. The most frequent used method of determining surface contamination is wipe sampling (McArthur, 1992). There are a lot of wipe sampling methods with different wiping materials (*e.g.* cotton or fibre-glass), different wiping methods (wet or dry) and different wiping surfaces (Brouwer *et al.*, 1995). It is not necessary or even desirable to remove 100% of surface residues, but to measure those residues which are likely to be transferred to human skin (transferable surface residues). Surface sampling can be considered a first approximation of personal exposure. If surface sampling and dermal exposure sampling are conducted simultaneously, a dermal transfer coefficient can be calculated for a specific work activity, and dermal exposure can be estimated subsequently from measurements of transferable surface residues (Fenske, 1993). Although surface wipe sampling is widely used in the field of radioactive contaminants, the methods applied are not standardized. Both the US Occupational Safety and Health Administration (Mc Arthur, 1992) and the Environmental Protection Agency (EPA, 1985) published general but vague methods for surface sampling. These methods provide information on the presence of the contaminants, but are highly variable and have unknown collection efficiency (Bierman *et al.*, 1995).

For this study it was decided to use a tracer for assessing the dermal exposure. To analyse the tracer, the VITAE (Video Imaging for Assessing Exposure) system is used. The advantage of using a tracer above analysing a substance from paint is that the composition of paint varies a lot with different paints, which hampers the choice of a substance in paint.

Appendix D Standard registration form (in Dutch)

Algemene meetgegevens

Informed consent getekend?	ja / nee
----------------------------	----------

Handeling

Begintijd	
Eindtijd	
Links- of rechtshandig	

Omgevingscondities

Temperatuur	
Aanzuigsnelheid (ivt)	
Effectiviteit afzuiging (rooktablet)	
Luchtvochtigheid	

Informatie spuiten

Object	binnenkant / buitenkant	
Druk		
Spuishopening		
Vorm straal		

Tankinhoud

Hoeveelheid verf	
Hoeveelheid verdunning	
Restant	
Viscositeit	
Tankmonsternummer	

Vitae handen

	Voor spuiten	Tussentijds	Na spuiten
Tijdstip			
Hands front right			
Hands front left			
Hands back right			
Hands back left			
Head front			

Spikes overall

	Monsternummer	Begintijd	Eindtijd
Spike			
Spike tankmonster			
Blanco			

Analyse

Vitae overall	Monsternr. vitae	Matrix	Chem.analyse ja/nee	Monsternr. chem.	Hoeveelheid wasbenzine
Right lower leg front		OVL BRO		-OVL-	
Right lower leg back					
Left lower leg front		OVL BLO		-OVL-	
Left lower leg back					
Right upper leg front		OVLBRB		-OVL-	
Right upper leg back					
Left upper leg front		OVL BLB		-OVL-	
Left upper leg back					
Head right		OVL HFD		-OVL-	
Head left					
Right forearm front		OVL ARO		-OVL-	
Right forearm back					
Left forearm front		OVL ALO		-OVL-	
Left forearm back					
Right upperarm front		OVL ARB		-OVL-	
Right upperarm back					
Left upperarm front		OVL ALB		-OVL-	
Left upperarm back					
Upper torso front 1		OVL TOV		-OVL-	
	2				
	3				
	4				
	5				
	6				
Upper torso back 1		OVL TOA		-OVL-	
	2				
	3				
	4				
	5				
	6				

Tijdregistratieformulier

Houding: 1=Rechtop 2=Gebogen 3=Links van object

4=Rechts van object 5=Recht ervoor

Tijdsintervallen	Afstand tot object	Houding	Opmerkingen
0			
5			
10			
15			
20			
25			
30			
35			
40			
45			
50			
55			
60			
65			
70			
75			
80			
85			
90			
95			
100			
105			
110			
115			
120			
125			
130			
135			
140			
145			
150			
155			
160			
165			
170			
175			
180			
185			
190			
195			
200			

Appendix E Calibration curves of uvitex OB and comparison of VITAE and chemical analysis

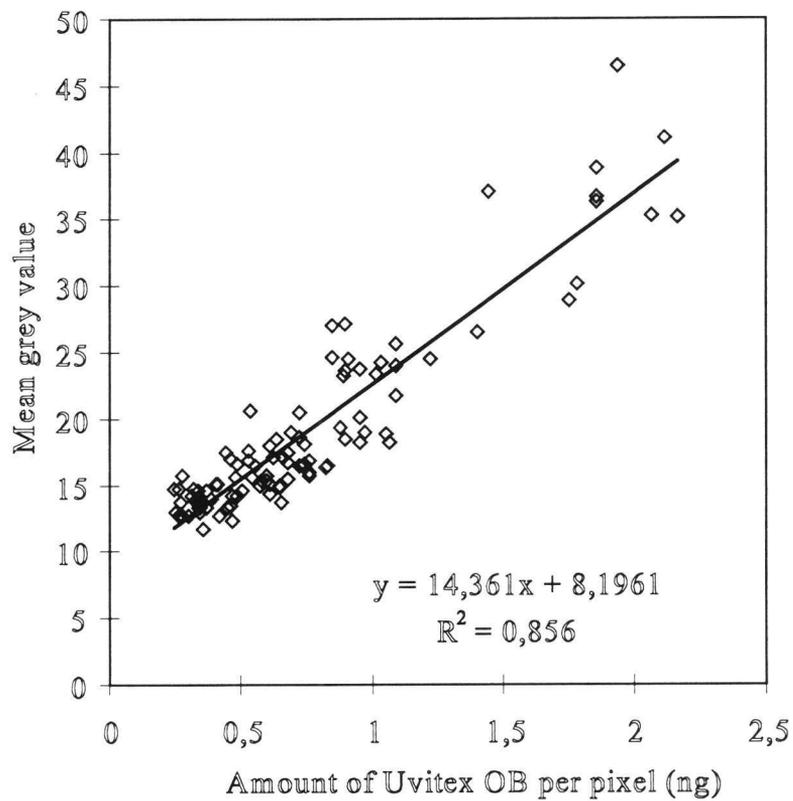


Figure E1 Calibration curve Uvitex OB on Tyvek

1. Calibration curves

The results of the spikes with Uvitex OB on Tyvek and consecutive image processing are plotted in figure E1, resulting in a calibration curve:

$$\text{Spot} = 8.20 + 14.36 * \text{Amount}$$

where:

Spot = grey value of the Tyvek after exposure

Amount = amount of Uvitex (ng)

Appendix E

Similar experiments were performed with Uvitex OB on skin, which revealed the calibration curve:

$$\text{Spot} = 6.15 + 8.62 * \text{Amount} + 2.01 * \text{Skin}$$

where

Spot = grey value of the skin after exposure

Amount = amount of Uvitex (ng)

Skin = grey value of skin before exposure.

2 Comparison of VITAE and chemical analysis

A comparison has been made between the exposure assessment of coverall parts by VITA and by chemical analysis. The results of both the pilot and the main study are plotted in figure E2 (n=43).

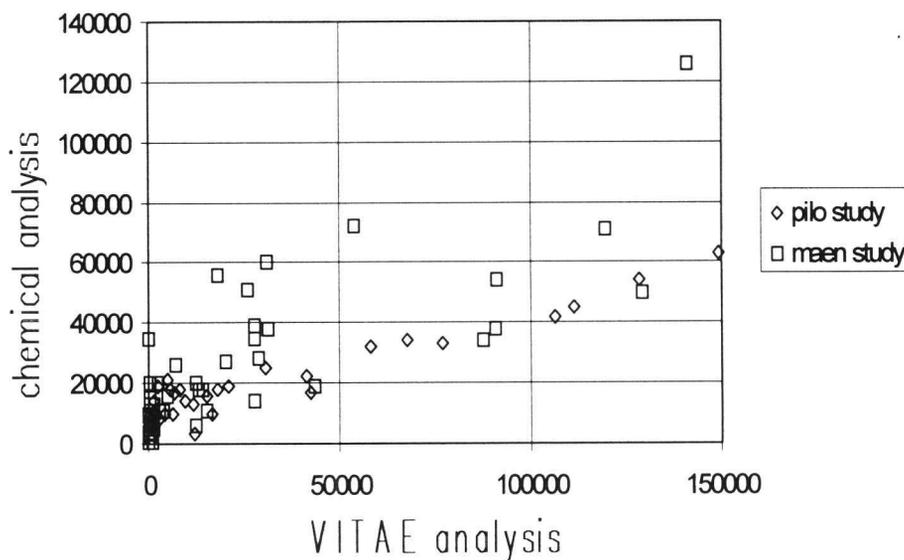


Figure E2 Plot of exposure assessment by VITAE and chemical analysis (n=43)

In 12 out of 43 coverall parts the exposure assessment by VITAE showed a higher exposure. Six out of these 12 VITAE images contained pixels above the range of quantification, whereas of the remaining 31 images only 2 contained pixel that were overexposed.

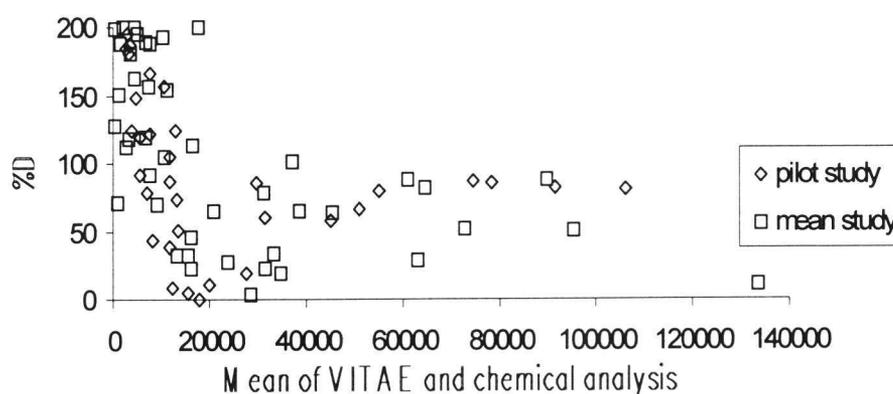


Figure E3 Percentage of difference of VITAE and chemical analysis

The mean of the chemical and VITAE analysis are also plotted against the percentage of difference (% D; figure E3). It is obvious that the difference is especially high at the lower range of the measured data.

Figure E4 shows a plot of the mean of the chemical and VITAE analysis against the difference. The mean of the differences is approximately -298 ng which does not statistically differ from zero. However, the interval between the limits of agreement, indicated by mean \pm 2SD is very large (approximately 90 mg), which indicates poor agreement between both methods. In the larger range of exposures there seems to be an overestimation by VITAE.

Appendix E

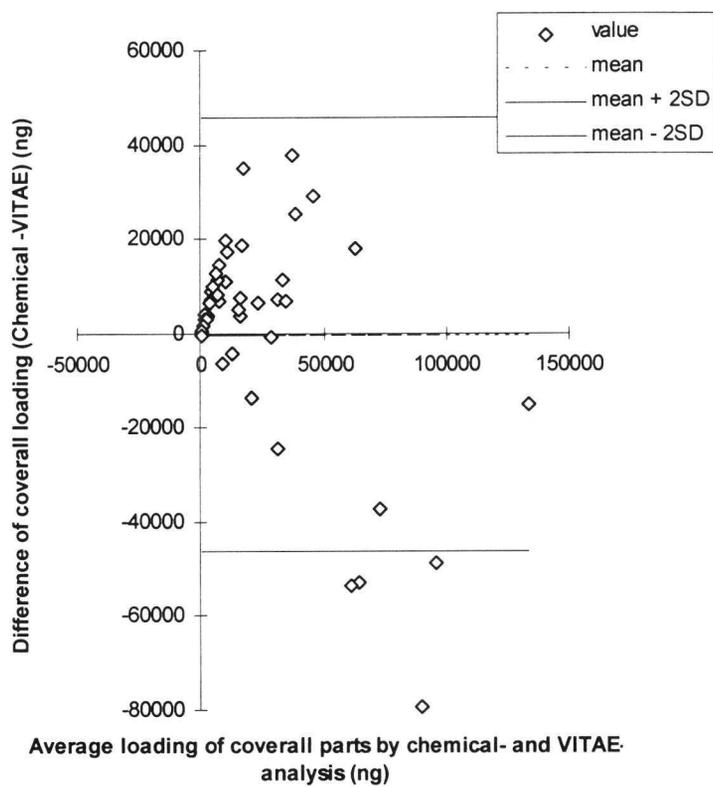


Figure E4 Mean against difference of exposure of overall parts by chemical- and VITAE analysis

Appendix F Schedule of chemical analysis per enterprise

Person	Coverall	Part(s) of the body
1	1	right forearm, torso back
	2	right lower leg, torso front
2	1	left lower leg
	2	left forearm
3	1	left upper arm, torso front
	2	left upper leg, torso back
4	1	right upper arm, head
	2	right upper leg

Appendix G Registered variables per enterprise (in Dutch)

BEDRIJF 1

Persoon	Binnen/buitenkant	Totale duur (min)	Spuitopening (μm)	Hoek straal (graden)	Hoevh. verspoten (L)	Links/rechts	Horizontaal/verticaal ^f
1	buiten	14	130	30	6.5	links	horizontaal
2	buiten	11	130	30	5.5	links	horizontaal
3	binnen	4	130	30	2.5	links	horizontaal
4	buiten	12	130	30	8	rechts	horizontaal
5	buiten	14	130	30	7.5	rechts	horizontaal
6	buiten	4	130	30	3	links	horizontaal
7	buiten	6	130	30	5	links	horizontaal
8	buiten	21	130	30	13	rechts	horizontaal
9	buiten	10	130	30	8	rechts	horizontaal

Persoon	(Af)stand t.o.v. object (m)	Deur(en)	Afzuiger	Gebogen rug ^a	Op knieën/gehurkt ^a	Trap ^b	Schoonspuiten spuit
1	1,0 recht voor	open	n.v.t.	ja	nee	nee	ja
2	1,0 recht voor	dicht	n.v.t.	ja	nee	nee	ja
3	1,0 recht voor	dicht	n.v.t.	ja	nee	nee	ja
4	0,8 recht voor	open	n.v.t.	ja	nee	nee	ja
5	0,8 recht voor	dicht	n.v.t.	ja	nee	nee	ja
6	1,0 recht voor	dicht	n.v.t.	ja	nee	nee	ja
7	0,9 recht voor	dicht	n.v.t.	ja	nee	nee	ja
8	1,0 recht voor	open	n.v.t.	nee	ja	nee	ja
9	1,0 recht voor	open	n.v.t.	nee	ja	nee	ja

^a bij het spuiten van de onderste helft van de container

^b bij het spuiten van de bovenste helft van de container

^c de spuitbeweging

BEDRIJF 2

Persoon	Binnen/buitenkant	Totale duur (min)	Spuitopening (μm)	Hoek straal (graden)	Hoevh. verspoten (L)	Links/rechts	Horizontaal/verticaal ^c
10	buiten, alleen zijkant	8	254	40	6	rechts	verticaal
11	buiten, alleen zijkant	4	254	40	3.5	rechts	verticaal
12	binnen	5	254	40	4	rechts	verticaal
13	buiten, alleen zijkant	9	254	40	6.5	rechts	horizontaal
14	buiten, alleen zijkant	12	254	40	7.5	rechts	horizontaal
15	buiten, alleen zijkant	16	254	40	8.5	rechts	horizontaal
16	buiten, alleen zijkant	10	254	40	5.5	rechts	horizontaal
17	binnen	9	254	40	5.5	rechts	horizontaal
18	buiten, alleen zijkant	11	254	40	7	rechts	afwisselend
19	buiten, alleen zijkant	8	254	40	50	rechts	verticaal

Persoon	(Af)stand t.o.v. object (m)	Deur(en)	Afzuiger	Gebogen rug ^a	Op knieën/gehurkt ^a	Trap ^b	Schoonspuiten spuit
10	0,5 rechterschouder er naar toe	dicht	uit	ja	nee	nee	ja
11	0,5 afwisselend rechter/linkerschouder	dicht	aan	ja	nee	nee	nee
12	0,5 afwisselend rechter/linkerschouder	dicht	aan	ja	nee	nee	nee
13	0,5 recht voor	open	aan	nee	ja	nee	nee
14	0,75 recht voor	dicht	aan	nee	ja	nee	nee
15	0,5-0,75 recht voor	dicht	aan	ja	nee	nee	ja
16	0,5-0,75 recht voor	open	aan	ja	nee	nee	nee
17	0,5-0,75 recht voor	open	aan	ja	nee	nee	nee
18	0,5-1,0 rechterschouder er naar toe	dicht	aan	ja	nee	nee	nee
19	0,5 rechterschouder er naar toe	dicht	aan	ja	nee	nee	nee

^a bij het spuiten van de onderste helft van de container

^b bij het spuiten van de bovenste helft van de container

^c de spuitbeweging

BEDRIJF 3

Persoon	Binnen/buitenkant	Totale duur (min)	Spuitopening (μm)	Hoek straal (graden)	Hoevh. verspoten (L)	Links/rechts	Horizontaal/verticaal ^c
21	binnen	6	330	65	6	links	verticaal
22	buiten	19	330	65	8	links	wisselend
24	binnen	9	330	65	6.5	rechts	horizontaal
25	buiten, alleen zijkant	13	330	65	5.5	rechts	horizontaal
27	buiten, alleen zijkant	12	330	65	9.5	afwisselend	verticaal
28	buiten, alleen zijkant	11	330	65	9	rechts	horizontaal
30	buiten, alleen zijkant	8	330	65	4	rechts	verticaal
31	buiten, alleen zijkant	8	330	65	3	rechts	verticaal

Persoon	(Af)stand t.o.v. object (m)	Deur(en)	Afzuiger	Gebogen rug ^a	Op knieën/gehurkt ^a	Trap ^b	Schoonspuiten spuit
21	1,0 met rechter schouder er naar toe	dicht	uit	ja	nee	nee	nee
22	1,0 recht voor	dicht	na zijkanten aan	nee	nee	ja	nee
24	1,0-1,25 recht voor	rechter 1,5m open	aan	ja	nee	nee	nee
25	1,5 recht voor	rechter 1,5m open	aan	nee	nee	ja	nee
27	1,0 recht voor	rechter open	onbekend	nee	nee	ja	nee
28	0,5-1,0 recht voor	rechter open	onbekend	nee	nee	nee	nee
30	0,75-1,0 rechter schouder er naar toe	rechter open	onbekend	nee	nee	ja	nee
31	1,0 rechter schouder er naar toe	rechter open	onbekend	nee	nee	ja	nee

^a bij het spuiten van de onderste helft van de container

^b bij het spuiten van de bovenste helft van de container

^c de spuitbeweging

Table 1: Statistical distribution parameters of total dermal exposure and dermal exposure per area exposed of the spray-hand and the non-spray-hand, after painting the outside of the container.

	n	Exposure						Exposure per area exposed					
		AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Spray-hand	21	3.9	7.0	0.8 ^a	11 ^a	0.0 - 27	0.0 - 14	0.8	0.8	0.6 ^a	2.5 ^a	0.1 - 2.7	0.0 - 1.8
Non-spray-hand	21	1.3	3.4	0.2 ^a	10 ^a	0 - 15	0.0 - 4.3	0.5	0.6	0.4 ^a	2.1 ^a	0.0 - 2.5	0.0 - 1.3

^a GM and GSD are calculated for n=18, three persons were left out because there was 'no exposure' (below the limit of detection).

Table 2a Statistical distribution parameters of total potential dermal exposure and potential dermal exposure per area exposed of the back and front of the coverall, during spray painting the outside of the object

	n	Exposure						Exposure per area exposed					
		AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Front ^d	21	105 ^a	86	64	3.5	2.1 - 301	13 - 185	0.8 ^b	0.3	0.7	1.7	0.1 - 1.5	0.4 - 1.1
Back ^d	21	35 ^a	39	14	6.5	0.1 - 151	1.1 - 73	0.4 ^b	0.2	0.4	1.6	0.1 - 1.0	0.2 - 0.6

Table 2b: Statistical distribution parameters of total potential dermal exposure and potential dermal exposure per area exposed of the back and front of the coverall, after spray painting the inside of the object

	Exposure						Exposure per area exposed						
	n	AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Front ^d	5	344	156	307	1.8	126 - 470	168 - 465	1.1 ^c	0.2	1.0	1.2	0.8 - 1.3	0.9 - 1.2
Back ^d	5	194	126	140	2.9	26 - 309	53 - 299	0.6 ^c	0.2	0.6	1.4	0.4 - 0.8	0.4 - 0.8

^a Significant difference ($p < 0.001$)

^b Significant difference ($p < 0.000$)

^c Significant difference ($p < 0.005$)

^d Hood is not included

Table 3: Percentage of the area exposed (coverall), related to the total area, given for several parts of the body, after painting the in- or outside of the container

	Percentage of the area exposed (%)					
	Outside (n=21)			Inside (n=5)		
	AM	SD	Range	AM	SD	Range
Lower legs	29	20	1.2 - 70	61	8.7	50 - 69
Upper legs	8.6	9.8	0.07 - 30	31	23	1.8 - 56
Torso	5.1	5.5	0.04 - 17	19	11	0.3 - 28
Forearms	9.3	9.7	0.0 - 30	28	14	4.5 - 36
Upper arms	4.0	5.6	0.0 - 19	23	14	2.0 - 37
Hood	8.2	11	<0.01 - 33	28	18	1.1 - 49
Total front ^a	12	8.1	1.5 - 27	31	14	9.3 - 43
Total back ^a	6.8	6.0	0.08 - 18	25	13	5.6 - 38
Total coverall	9.3	6.9	0.8 - 22	28	13	7.2 - 40

^a Hood not included

Table 4: Percentage of the area exposed (skin), related to the total area, given for several parts of the body, after painting the in- or outside of the container

	Percentage of the area exposed (%)					
	Outside (n=22)			Inside (n=5)		
	AM	SD	Range	AM	SD	Range
Hands	9.5	12	(0.0 - 41)	17	11	(4.0 - 32)
Head	1.1	3.1	(0.0 - 15)	1.5	2.4	(0.0 - 5.6)

Table 5: *Statistical distribution parameters of the exposure to the hands.*

	Exposure (μg)				
	n	AM	SD	Range	10-90 perc.
Inside	5	11	11	1.6 - 30	3.4 - 22
Outside	22	7.3	13	0 - 51	4.4 - 19

Table 5b: *Statistical distribution parameters of the dermal area dose for the exposed parts of the hands.*

	Exposure (ng/mm^2)				
	n	AM	SD	Range	10-90 perc.
Inside	5	1.2	0.5	0.8 - 2.0	0.9 - 1.7
Outside	22	0.9	0.8	0 - 3.1	0.1 - 1.9

Table 6a: *Statistical distribution parameters of coverall area dose for the total coverall area.*

	Exposure per total coverall area (ng/mm^2)				
	n	AM	SD	Range	10-90 perc.
Inside	21	0.06	0.06	0.001-0.2	0.1 - 0.3
Outside	5	0.24	0.12	0.07-0.4	0.01 - 0.1

Table 6b: *Statistical distribution parameters of skin area dose for the total skin area.*

	Exposure per total skin area (ng/mm^2)				
	n	AM	SD	Range	10-90 perc.
Inside	22	0.13	0.25	<0.001-1.0	0.06 - 0.4
Outside	5	0.19	0.20	0.03-0.6	0.002 - 0.4

AM: Arithmetic Mean 10-90 perc. 10 to 90 percentile
SD: Standard Deviation

Appendix I Dermal exposure at different workplaces

Table 1a: Statistical distribution parameters of total potential dermal exposure and potential dermal exposure per area exposed (coverall) after painting the outside of the container, given for the different workplaces

	n	Exposure						Exposure per area exposed					
		AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Workplace A	8	154	156	83	3.8	11 - 471	21 - 302	0.7	0.2	0.7	1.4	0.4 - 1.4	0.5 - 1.0
Workplace B	7	115	70	100	1.7	44 - 256	65 - 185	0.6	0.2	0.7	1.4	0.3 - 0.8	0.4 - 0.8
Workplace C	6	166	150	68	7.4	2.2 - 397	10 - 326	0.6	0.3	0.5	2.1	0.1 - 0.9	0.3 - 0.9

Table 1b: Statistical distribution parameters of total dermal exposure and dermal exposure per area exposed (skin) after painting the outside of the container, given for the different workplaces

	n	Exposure						Exposure per area exposed					
		AM (μg)	SD	GM (μg)	GSD	Range (μg)	10th-90th perc. (μg)	AM (ng/mm^2)	SD	GM (ng/mm^2)	GSD	Range (ng/mm^2)	10th-90th perc. (ng/mm^2)
Workplace A	8	0.3 ^a	0.4	0.04	13	0.0 - 1.1	<0.01 - 0.8	0.4 ^{bc}	0.4	0.3	2.3	0.1 - 1.1	0.1 - 0.7
Workplace B	8	10 ^a	11	5.0	4.2	0.5 - 33	1.2 - 20	1.2 ^b	0.7	1.0	1.9	0.4 - 2.3	0.6 - 2.0
Workplace C	6	13	20	1.6	17	0.06 - 52	0.1 - 36	1.2 ^c	1.2	0.8	2.7	0.2 - 2.9	0.3 - 2.4

^a significant difference A and B ($p < 0.002$)

^b significant difference A and B ($p < 0.006$)

^c significant difference A and C ($p < 0.028$)

Appendix J Determination and including of a LOD

In this appendix the derivation of the LOD is given, also the impact of including the LOD is studied.

The coverall parts for which the VITAE system gave a higher exposure than the chemical analysis were not considered (12 images of in total 44 images). From the other coverall parts, the difference between the VITAE and the chemical analysis and the difference between the total area and the area exposed was calculated. The difference of the chemical and the VITAE analysis was divided by the difference between the total area and the area exposed. This division resulted in an amount of Uvitex OB per mm^2 on the area which was observed by VITAE as non exposed. This concentration might be considered as an estimate of a LOD. The mean concentration, calculated by this procedure, is 0.06 ng/mm^2 , with a minimum of 0.0009 ng/mm^2 and a maximum of 0.16 ng/mm^2 . The mean concentration (0.06 ng) and the highest concentration (0.16 ng) will be used to observe the impact of including a LOD in the non-detectable parts of the all the total coveralls analysed by VITAE.

When a LOD of 0.16 ng/mm^2 is assumed, the mean exposure (on the coverall) after spraying the outside of the container is calculated to be $311 \text{ }\mu\text{g}$, with a range of 171 to $624 \text{ }\mu\text{g}$ ($n=21$). VITAE measured a mean exposure (on the coverall) of $144 \text{ }\mu\text{g}$ with a range of 2 to $470 \text{ }\mu\text{g}$. In the above mentioned calculation a value of half the LOD is assumed to be present on the non-detectable parts of the coverall ($= 0.08 \text{ ng/mm}^2$). Using the same LOD, the range of exposure, after painting the inside of the container is calculated as 314 to $939 \text{ }\mu\text{g}$, with a mean of $689 \text{ }\mu\text{g}$ ($n=5$). The VITAE system measured an exposure which varied from 151 to $806 \text{ }\mu\text{g}$ (mean was $558 \text{ }\mu\text{g}$).

When a LOD of 0.06 ng/mm^2 is assumed the mean exposure during painting the outside of the container is calculated as $207 \text{ }\mu\text{g}$ with a range of 528 to $656 \text{ }\mu\text{g}$. Using the same LOD, the mean exposure after painting the inside of the container is calculated as $607 \text{ }\mu\text{g}$, with a range of 212 to $855 \text{ }\mu\text{g}$ (using the half of the LOD = 0.03 ng/mm^2 on the non-detectable area). The impact of introducing a LOD is less when the exposed area is larger. This can be concluded in view of the difference between the 'non-corrected' and the 'corrected' exposure values after painting the inside of the container (mean exposure using LOD of $0.16 \text{ }\mu\text{g}$ increased with 23%) which is less than the difference for the 'corrected' and 'non corrected' exposure values after painting the outside of the container (mean exposure using LOD of $0.16 \text{ }\mu\text{g}$ increased with 116%). The observed exposed area, analysed by VITAE, is highest for painting the inside of the container.

To be able to use the exposure values for risk assessment purposes, the measured dermal exposure values must be translated into exposure to certain non-volatile compounds in paint. This is only possible when it is assumed that

Appendix J

Uvitex OB behaves like a non-volatile compound in paint: the vapour pressure of Uvitex OB is very low (2.5×10^{-8} Pa at 20°C) and the Uvitex is assumed to be dissolved in the paint fully and homogeneously.

Below, the dermal exposure will be estimated in which a non-volatile compound in paint of 10% is assumed. This calculation is only performed for the main study.

The mass percentage of Uvitex OB in the paint was 0.0074%. When a mass percentage of a non-volatile compound in paint is assumed to be up to 10%, the measured amounts of Uvitex OB (Table 4.7) must be multiplied by $10/0.0074=1351$.

The (potential) dermal exposure for a non-volatile compound in paint, with a concentration of 10% in paint is therefore calculated as follows:

- skin exposure (face, hands), after painting inside: 2 - 42 mg;
- skin exposure (face, hands), after painting outside: <0.02 - 70 mg;
- dermal exposure (coverall), after painting inside: 205 - 1090 mg;
- dermal exposure (coverall), after painting outside: 3 - 636 mg.

To study the impact of including a LOD, the exposure on the coverall is calculated by assuming a LOD of 0.16 and $0.06 \mu\text{g}/\text{mm}^2$. When an amount of half the LOD of $0.16 \mu\text{g}/\text{mm}^2$ is considered on the non-detectable parts of the coverall, the total potential exposure on the coverall is calculated as:

- ▶ painting inside: 426-1268 mg
- ▶ painting outside: 232-844 mg

When a LOD of $0.06 \mu\text{g}/\text{mm}^2$ is considered, the total potential exposure on the coverall is calculated as:

- ▶ painting inside: 287-1156 mg
- ▶ painting outside: 88-714 mg

The mean exposure on the coverall calculated from VITAE after painting the in- and outside of the container is 754 and 194 mg respectively. The mean exposure, corrected for a LOD of $0.16 \mu\text{g}/\text{mm}^2$ is 930 and 420 mg respectively (increase is 23% and 116%), and corrected for a LOD of $0.06 \mu\text{g}/\text{mm}^2$, 820 and 280 mg respectively (increase is 9% and 44%).

Considering the above exposure values, it appears that including a LOD on the non-detectable parts of the coverall is of minor influence. The range of the exposure is still in the same order of magnitude. The influence is highest at the lower end of the range, this is probably there were the exposed area is the smallest. For the pilot study this influence will be probably be even less, since the observed exposed area was higher.

For the skin exposure no LOD could be included. It was not possible to determine a LOD, such as for the coverall.