Harpur Hill, Buxton
Derbyshire, SK17 9JN
T: +44 (0)1298 218000
F: +44 (0)1298 218590
W: www.hsl.gov.uk

HEALTH & SAFETY LABORATORY

Protective glove selection for workers using NMP containing products -Graffiti removal

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Project Leader: **Dr. Vincent Crook (PhD)**

Author(s): **Dr. Vincent Crook (PhD) & Mr. Andrew Simpson (BSc)**

Science Group: **Exposure Control and Measurement**

FOREWORD

A previous study conducted by HSL in collaboration with the N-Methyl Pyrrolidone Producers Group Inc. presented quantitative data on potential dermal exposure to N-methyl pyrrolidone (NMP) that was gathered for the purpose of validating and improving predictive models generated by the EU RISKOFDERM project. This project was conceived as a response to the apparent risk of dermal exposure inherent in the task of graffiti removal. Exposure to the hands was a particular concern.[1, 2]

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EXECUTIVE SUMMARY

Objectives

N-Methyl Pyrrolidone (NMP) (CAS Number 872-50-4) is a powerful solvent that is able to solvate compounds that would otherwise be immiscible and difficult to handle and process. It finds use in graffiti removal formulations. In the plastics industry, it is used as a solvent for natural and synthetic polymers. In the agricultural industry, NMP is currently in use as a co-formulant in a range of biocides including; fungicides, pesticides, herbicides and seed treatments. Often NMP is a major component of the formulation (< 70 %). NMP is also used in the large-scale recovery of hydrocarbons from industrial processes and is intrinsic in many cleaning processes in the electronics industry.

In this work HSL intended to test a range of readily available chemically resistant gloves against actual graffiti removal formulations in order to inform glove selection and study the competing influences upon chemical resistance of glove type and solvent formulation. The initial phase of this work involved screening for the suitability of gloves against NMP and graffiti removal formulations. Gloves were selectively tested against four NMP containing formulations (GC 300, Blitz GS, Graffiti Gone CR-GR1 and DSI 6000) and pure NMP. Sceening tests involved visual assessment of glove condition following four hours of contact with a chemical, and a 24-hour gravimetric method of assessing solvent uptake by samples of gloves. This was followed by assessment of the resistance to permeation of some of the glove types using a continuous contact test based on the BS EN 374-3.

Main Findings

20 glove types were tested against NMP and relevant NMP containing formulations. This work has demonstrated that testing of gloves against NMP containing formulations rather than just pure NMP is necessary. With this in mind, the authors have demonstrated the chemical durability of the North Silver Shield glove against NMP and the NMP based formulations GC 300, DSI 6000, Blitz GS and Graffiti Gone CR-GR1 in swelling tests. Unfortunately these gloves can be awkward to work in; therefore Butyl rubber gloves may be by some workers. In swelling tests the butyl rubber type glove examined in this work (KCL Butoject 898) had good resistance to NMP, GC 300, DSI 6000 and Graffiti Gone CR-GR1 but not to Blitz GS. Blitz GS is an appreciably more aggressive product that is designed to solvate metallic paints but has ingredients in common with most other graffiti removal products. The best performing gloves tested in continuous contact permeation tests were the North Silver Shield (T) and KCL Butoject gloves (J), which resisted continuous contact permeation for over eight hours when tested against both NMP and the commercial cleaning product Graffiti Gone CR-GR1.

Of the other glove types tested, the Latex gloves demonstrated some potential chemical resistance in swelling tests against NMP but less resistance to the NMP containing formulations. It is possible that further testing could establish these gloves as ‘splash resistant’ and, if used, they should be replaced on a task-by-task basis and immediately when known to be contaminated.

It was hypothesised that the 4-hour screening and 24 hours gravimetric solvent uptake tests conducted in this work may be a cost effective way of assessing gloves in less well equipped laboratories. This has been demonstrated in part, however a thin polyethylene Ansell ProFood glove passed both of these tests and failed the BS EN 374-3 continuous contact permeation test. Therefore, it is only possible to say that these are useful ‘indicator’ and ‘screening’ tests that could preclude some glove types from further testing or could even be carried out by inspectors shortly after a visit to a site that was thought to be using unsuitable gloves with chemicals. In this work, these two screening tests eliminated 17 glove types from further investigation (although the authors tested three of these for other reasons). The 4-hour observational screening test performed in this work proved appreciably powerful. In this work it eliminated 12 gloves from further investigation. It is worth noting that this test could be carried out on site simply by turning the finger of a glove inside out and pipetting some chemical into it. A handy way of visualising the permeating chemical is to use permeatec pads, these blacken when in contact with solvent, or alternatively, to put some blue roll tissue in contact with the 'dry' side of the glove –when the chemical permeates it dampens the blue roll tissue and it turns dark blue.

Of the gloves that were reported to be used by graffiti workers, the nitrile gloves were found to be unsuitable for use with pure NMP in BS EN 374-3 continuous contact permeation tests due to rapid degradation allowing a high permeation rate (32 $\mu g.cm^{-2}min^{-1}$ in the case of reusable nitrile gloves and >26 $\mu g.cm^{-2}min^{-1}$ in the case of a single use disposable nitrile glove type), which leaves them physically weakened. An example of a thin latex type glove was also unsuitable for use with pure NMP due to very short breakthrough time (~2 mins) and a high permeation rate of > 34 $\mu g.cm^{-2}min^{-1}$.

Recommendations

- It is recommended that North Silver Shield (layered polyethylene/ethane-vinyl alcohol) gloves (or similar) can be used to provide adequate protection when handling NMP containing products.
- Butyl gloves, used with caution, would be a second choice. In addition Butyl gloves offer advantages in dexterity and robustness.
- It is recommended that gloves be tested against all relevant chemical formulations as a matter of routine in order to inform glove selection.
- Assumptions of glove choice based on the use of model compounds or similar formulations should be made with extreme caution.
- The two screening tests used in this work proved useful indicator methods to speed up and minimise the cost of this testing gloves.
- The BS EN 374-3 continuous contact test and it successors should remain the benchmark for chemically protective glove type decisions.
- It is recommended that, when necessary and feasible, gloves be tested for suitability by inspectors on site using the 4-hour observational screening test.

1 INTRODUCTION: JUSTIFICATION FOR THE WORK

1.1 NMP USE

N-Methyl Pyrrolidone (NMP) (CAS Number 872-50-4) has been manufactured on a commercial scale since the 1960s.[3] Its current production in the EU is 38,000 tonnes.[4] The pH of NMP is typically between 8 and 9.5. It is a colourless liquid with a mild amine odour. Its most attractive property is its high polarity –it is a very good solvent. As a powerful solvent it is able to solvate compounds that would otherwise be immiscible and difficult to handle and process –hence the use of NMP as a solvent to graffiti. In the plastics industry it is used as a solvent for natural and synthetic polymers. Its miscibility with water facilitates the spinning of acrylic fibres directly from the solvent of polyacrylonitrile's manufacture. In the agricultural industry NMP and NMP derivatives are currently in use as co-formulants in a range of biocides including; fungicides, pesticides, herbicides and seed treatments.[5, 6] Often NMP is a major component of the formulation (~70 %). NMP is also used in the large-scale recovery of hydrocarbons from industrial processes and is intrinsic to many cleaning processes in the electronics industry.

1.2 SUMMARY OF PREVIOUS WORK ON GRAFFITI WORKERS

A previous report based on a study that was conducted by Roff *et al.* in collaboration with the N-Methyl Pyrrolidone Producers Group Inc. presented quantitative data on potential dermal exposure to N-methyl pyrrolidone (NMP).[1, 2] The NMP containing cleaning agents were found to be unpopular with the workforce because they dissolved their protective gloves. Their gloves were either latex disposable, nitrile disposable gloves, or heavier unlined black nitrile gloves. At one site, cotton-lined nitrile gloves were worn. Some of these gloves were clearly unsuitable for the task because they dissolved quickly. Graffiti workers were found to perform five tasks involving NMP product use. These were: (a) brushing on of the product, (b) spraying off with a water jet, (c) hand spraying on of the product, (d) wiping on the product and (e) wiping off the product. For the brushing task, all five subject's cotton hand samplers were moderately contaminated by up to 8 mg cm^{-2} of product. Those workers conducting task b received only slight hand contamination because the subjects were spraying clean water at the fluid that had been brushed onto the wall. All hand samplers were slightly contaminated (up to 0.4 $mg.cm^{-2}$ of product). For those subjects carrying out a hand trigger spray on (c) followed by a hand wipe off task (e) it was found that hand contamination was high for all subjects (1.5–33 $mg.cm^{-2}$ of product), which may be attributed to contact with the cloth used to wipe off the product, or to dribbles from the trigger spray. A wiping on and off task (d followed by e) was found to produce similar exposures to that of a hand spray on followed by a hand wipe off. This indicated that the hand-held trigger spraying part of the task contributed little compared with the wiping. PBPK modelling of biological monitoring results of the same graffiti workers showed that the measured inhalation exposures could not account for the levels of 5-HNMP in urine for some of the subjects. Therefore it was thought that systemic exposure through the dermal route was occurring despite the use of PPE. The lag in the time course of urinary concentrations of 5-HNMP (pre-shift next day biological monitoring samples were frequently higher than the corresponding post-shift samples) is also indicative of dermal exposure.

In a series of papers Anundi *et al.*[7-9] examined worker exposure to a range of solvents (including NMP) during graffiti removal tasks in Sweden. Air and biological monitoring were performed but there was no quantitative assessment of dermal exposure. Anundi *et al.* observed air concentrations of NMP ranging from 0.03 to 4.52 mg m^{-3}. Contrary to the findings of Roff *et al.* the authors describe the spraying off task as high risk, owing to the production of NMP containing aerosol, which was observed to stain the skin and clothes. Urinary levels of the metabolite 5-HNMP were found to be on average 3.31 $mmol.mol^{-1}$. In the study, the use of gloves varied considerably: on the day of sampling 87 % of workers used gloves and these were rarely of the solvent protective variety –butyl rubber gloves being the stated preferred option. Workers wearing gloves and/or respiratory masks during graffiti removal were found to exhibit significantly lower urinary levels of the NMP metabolite 5-HNMP. Unfortunately a comparison for the use of gloves alone was not presented. The report presents the health effects of NMP use: In comparison with depot workers, graffiti removers had a higher occurrence of rashes on hands and arm, rashes on face and neck, itching on hands or arms and irritated eyes.

To date there is a set of publications studying the skin penetration, metabolic pathways and inhalation by biological monitoring often using volunteer study.[4, 10-15] For example, a volunteer study by Åkesson and Johnson [10] exposed individuals to atmospheres of up to 50 mg m^{-3} for 8 hours and found a linear correlation between the amount of NMP inhaled and the metabolite 5-HNMP in urine collected during the last two hours of exposure. At HSL, scientists have studied the dermal penetration of aqueous NMP solutions in the laboratory by biological monitoring, this work reinforces the knowledge that NMP is easily absorbed through the skin.[14-16] Bader *et al.*[4] used urinary excretion rates from their own volunteer study to evaluate the graffiti removal exposure results of Anundi et al.[7] in order to illustrate the high dermal absorbivity of NMP. They concluded that the inhalation dose of 100 mg, found by Anundi *et al.* to occur from an 8 hour shift, might be absorbed through only a 10 cm^2 area of skin in only two hours.

1.3 SPECIFIC HEALTH EFFECTS CONCERNS RELATING TO WIDESPREAD NMP USE

According to HSE [17], NMP has an 8 hr workplace exposure limit of 25 ppm or 103 mg m^{-3} and 15 minute exposure limit of 75 ppm or 309 mg m^{-3}. It has the risk phase R36/38 meaning that it is classed as irritating to eyes and skin. The notation 'Sk' means that the substance can be absorbed through skin and that there are concerns that dermal absorption will lead to systemic toxicity. Rat studies have indicated that NMP may be a reproductive toxic compound,[18] whilst studies reviewed by the World Health Organisation [19] have shown that rats exposed to NMP exhibited severe major organ effects, weight loss and a massive increase in mortality. There is no data for repeated dose effects in human subjects.

Although the skin irritant issues related to NMP are known, they are perhaps not immediately dramatic or striking enough to trigger a health and safety led push for change. This is a dangerous situation because reaction to the solvent can often be quite rapid and severe. For example, Leira *et al*. [20] reported that within two days of switching to NMP use 10 out of 12 employees in a small Norwegian electro-technical company were showing symptoms of acute irritant contact dermatitis. The largest health risk from NMP use is probably its use as a coformulant for other more hazardous active ingredients. In fact, NMP rarely find use in its pure form and even when it does the result of its use is often an NMP solution of another product. For example, when NMP is used as a solvent to polymer manufacture, the resultant polymer dope will contain NMP, polymer, initiators and unreacted monomer (the building blocks of polymers). In the case of acrylic polymer manufacture, the monomer is acrylonitrile – a toxic substance. Given NMP's propensity to penetrate the skin it is clear that the mixture of NMP and acrylonitrile may be more hazardous to use than its constituent parts. The risk of

NMP increasing the dermal penetration of toxic products is also high in the field of agriculture where NMP finds use as a coformulant in fungicides, pesticides, herbicides and seed treatments.[6] It is the opinion of the authors that the personal protective equipment (PPE) used by agricultural workers, including gloves and disposable suits is unlikely to offer sufficient resistance to NMP penetration.

Owing to the interest in the skin as a site of drug application for both the local and the systemic effect, there is a body of recent work studying the skin penetration of drugs from NMP solution. Here, the high skin penetration flux and the relatively low health risks from a single dose of NMP are put to good use. Penetration enhancement of the drug is commonly reported. For example, Akhter and Barry [21] reported a sixteen-fold increase in the penetration flux of ibuprofen when NMP was included at only low concentrations (0.05-5 %) in their formulation.

1.4 NMP AND GLOVES

That NMP should have a high permeation rate through many gloves is unsurprising. NMP is a good solvent to many man-made polymers and it will readily swell others. Swelling will often occur in cross-linked polymers in the place of solublisation. The German glove manufacturer KCL has data available on the permeation of pure NMP through all of their glove products available at http://www.kcl.de. This data is summarised in Table 1.1. Only the two butyl based KCL gloves are reported to be suitable for use for an 8 hr (480 min) shift when contact with pure NMP is possible. According to the website http://physchem.ox.ac.uk/MSDS/glovesbychemical.html, which lists common chemicals and the gloves that should be worn when handling them, only butyl and polyethylene/ethene vinyl alcohol (PE/EVAL) gloves are stated as resistant to NMP. The Ansell Edmont Chemical Resistance Guide [22] states that, of their chemical resistant gloves, their Barrier™, Natural Rubber (Canners™) and Neoprene/Natural Rubber blend (Chemi-Pro™) gloves are well suited to application with NMP. Worryingly none of the graffiti workers observed in HSL's own study were wearing particularly NMP-resistant gloves, their gloves were either latex disposable, nitrile disposable gloves, heavier unlined black nitrile gloves or cotton-lined nitrile gloves.[1] Considering that nitrile glove use was common in HSL's study and that nitrile gloves are often regarded as the glove of choice for chemical protection, the apparent lack of protection that is offered by nitrile gloves to pure NMP is concerning (a breakthrough time of 0 mins is reported by KCL).

Table 1.1 Summary of the permeation of pure NMP through KCL's glove products

KCL Code	Brand	R = reusable S = single use	Material	Breakthrough time of neat NMP (min)	Thickness (mm)
KCL 898	Butoject	R	Butyl rubber	480	0.7
KCL 897	Butoject NEU	R	Butyl rubber	480	0.3
KCL 890	Vitoject	R	Viton	60	-
KCL 395, 403, 465	Natural latex	R	Natural latex	240	1
KCL 706, 708	Natural latex	-	Natural latex	60	0.6
KCL 727	Neoprene nitrile I	-	Neoprene nitrile	120	-
KCL 717	Neoprene nitrile II	-	Neoprene nitrile	60	0.7
KCL (many codes)	Nitrile I	R	Cotton lined nitrile	30	-
KCL 740, 741	Nitrile II	S	Nitrile	0	0.11
KCL 743	Nitrile III	S	Nitrile	0	-

A number of studies concerning the permeation of NMP through gloves have been published in the academic literature. Zellers and Sulewski [23] studied the temperature dependence between 25 – 50 ^{o}C of NMP permeation through butyl and natural rubber gloves. The butyl gloves tested (North B161) were found to be resistant for the duration of the four-hour experiment and showed no break through at any of the temperatures tested. The Edmont, Pioneer and Ansell natural rubber gloves that were tested displayed breakthrough times of between 42 and 57 mins that decreased by factors of 7-10 at elevated temperatures. Zellers has also modelled NMP permeation through Viton gloves based on experimental studies of solvent uptake.[24]

Unfortunately for those using NMP in the workplace, glove selection is not as simple as it may seem. Material safety data sheets (MSDS) often do not specify a glove to use with the product, stating; 'use suitable gloves' or 'use chemical resistant gloves'. The specific advice in the MSDSs given to users about glove use and skin protection when using the Graffiti products that this study investigates is displayed in Table 1.2. When they are specified, the MSDSs recommend rubber, neoprene and butyl gloves but don't state the thickness of gloves that should be used or the duration of protection that such gloves offer.

An additional confusion to correct glove selection is that when NMP is used as a mixture with coformulants, its permeation through gloves cannot be easily predicted. When Nelson *et al.*[25] studied glove permeation of 29 common laboratory solvents they found five different types of permeation behaviour. Of the two mixtures they tested, one showed a significant synergistic effect in comparison with its components alone resulting in an earlier breakthrough than predicted. In Klinger and Boeniger's [26] critique of assumptions about selecting chemical resistant gloves the authors refer to several studies concluding that is it necessary to test products alone and as a mixture in combination with other substances in the work area.

In a comparable study to that of this project, Stull *et al.* [27] studied permeation resistance of twenty glove types to several commercial paint stripping formulations using ASTM test method F 739. In this test the NMP containing products were generally less penetrative than those containing dichloromethane (DCM), acetone, methanol, toluene and *iso*-propanol. The authors also found that the results of testing gloves against specially prepared simplified 'surrogate' paint stripper formulations had little relation to results of testing of gloves against actual paint stripping products. This reinforces the need for testing the actual products against gloves before glove selection takes place. In Stull's paper no gloves were tested beyond 4 hours.

Table 1.2 NMP containing Graffiti removal formulations and MSDS details. Those in **bold** are tested against gloves in this work

Brand	**MSDS REF**	**Safety Data on MSDS relating to PPE**	**Formulation (%)**
GRAFFSOLVE GEL SF A versatile graffiti remover in gel form for use on vertical and downward facing surfaces.	08/03/01 No 2	Wear gloves and safety goggles when handling or applying the product.	Citrus terpenes 30-60 %, N-Methyl 2-pyrrolidone 10-30%, Non-ionic surfactants 5-15%. A mixture of glycol ethers, thickeners and non-ionic tensides.
GRAFFSOLVE LIQUID LT. A liquid blend of solvents for graffiti removal. Effective against a wide range of inks and paints.	08/03/01 No 2	Wear solvent resistant gloves and safety glasses when handling or using the product.	Citrus terpenes 30-60% N-Methyl 2-pyrrolidone 10-30% Non-ionic surfactants 5-15%
BLITZ GS (METALLIC PAINTS)	**16/1/03**	**Use rubber or chemical resistant gloves.**	**N-Methyl-2-pyrrolidone 50 – 80 %** **D'limonene 20 – 40 %**
AGS Graffi Clean 300 no. 3265 (GC 300)		**Use neoprene or rubber gloves**	**N-Methyl 2-pyrrolidone 5-10%,** **3-butoxypropan-2-ol 5-10%,** **Gamma butylactone 20-30%,** **Monoisopropylamine 1-5%,** **Salt of dodecyl benzene sulphonic acid**
Heritage Preservation Ltd	17/11/03	Gloves resistant to chemical products (butyl and neoprene rubbers).	N-Methyl 2-pyrrolidone 30 – 40 % Tetrasodium salt of ethylenediamine tetraacetic acid < 5 % 1-methoxy-2-propanol < 5 % Sodium metasulfate < 5 %
MPGRG (1) LONDON UNDERGROUND PART NOS: 17418/141 & 17418/142 Multi-purpose Graffiti Removing gel	05/08/03 No: 1	Wear rubber (not PVC) gloves and overall.	2-methoxy-1-methylethyl acetate 10-30% 3-buxtoxypropan-2-ol < 10 % Non-ionic Surfactant < 10 % N-Methyl 2-pyrrolidone 30-60 % Orange terpenes < 10%
Graffiti Remover Safe on Plastics. Graffiti Remover Safe on Plastics (SOP) has been developed specifically for use on sensitive surfaces such as Plastics and Polycarbonates, surfaces which would normally be attacked by most other Graffiti removers.	18/01/01 No: 2	Hand protection: Protective gloves. Eye protection: Safety goggles. Skin protection: Protective clothing with elasticated cuffs and closed neck. Boots made of PVC.	N-Methyl 2-pyrrolidone 30-60 % 2-(2-butoxyethoxy) ethanol 10-30 % 1-phenoxy-2-propanol < 10 % Orange terpenes <10 % Non-ionic surfactants < 20 %
Graffiti Gone CR-GR1 **LONDON UNDERGROUND PART NO: 17418/147**	**14/03/05 No: 6**	**Wear rubber (not PVC) gloves and overalls. Hand protection: Butyl gloves. Neoprene gloves. Skin protection: Protective clothing with elasticated cuffs and closed neck.**	**N-Methyl 2-pyrrolidone 30-60 %** **2-(2-butoxyethoxy) ethanol 10-30 %** **1-phenoxy-2-propanol < 10 %** **Orange terpenes < 10 %** **Non-ionic surfactants < 20 %**
GR II biodegradable paint and adhesive remover	14/06/02	Personal Protective Equipment: Have available and wear as appropriate: gloves, safety glasses and apron.	Water < 5 % Methyl esters >70 % N-Methyl-2-pyrrolidone < 30 % Lauramine Oxide < 2 %
DSI 6000 GR		**The use of neoprene rubber gloves is recommended**	**NMP 20-30 %** **Gamma-butyrolactone < 20 %** **Glycol ether 40-60 %**

1.5 GRAFFITI PRODUCTS AVAILABLE IN THE UK

Given the health risks of NMP mixtures this study concentrates upon the PPE penetration of commercial graffiti removal products, which commonly contain a handful of ingredients. An internet search of available graffiti removal products was performed at the inception of this project using http://www.google.co.uk/, http://www.ask.com/ and http://www.alltheweb.com/ using the terms graffiti removal, graffiti remover and graffiti NMP plus other variants. Those products available outside of the UK were discounted, as were those available in aerosol spray form and as disposable wipes. The ten products that contain NMP are displayed in Table 1.2. Examination of ingredients of each product reveals that the precise amounts of each coformulant are often displayed as a broad range and that the sum of the ingredients often adds up to less than 100 %. This is probably because the mass balance is water. Work with rats has indicated that dilution of NMP with water decreased skin absorption.[28] The concentration of NMP will clearly have a bearing upon the skin penetration of the graffiti product. Of relevance is work by Lee et al. [29] who reported that in human volunteers dermal drug delivery was significantly enhanced in aqueous systems above 80 % NMP. In this range, drug flux was found to correlate with NMP flux. Table 1.3 features a list of the chemicals found as coformulants of NMP in UK graffiti removal products. When available the risk phrases that were featured in the MSDS or found at http://physchem.ox.ac.uk/msds/ are displayed in the table. Of the coformulants, the majority have been associated with a skin or eye irritant effect –which is a significant health concern. An additional health concern is the use of terpenes, which have been observed by Kakubari-Ikuhiro *et al.* (REF) to give ‘remarkable’ skin penetration enhancement and can be skin sensitisers.

Table 1.3 List of coformulants found in commercial NMP-containing graffiti products and their health risks

Co-formulant	**Comment**	**Risk phrases obtained from reference tables**	
Citrus terpenes, Orange terpenes, D-limonene	Extract of citrus fruit used in cleaning products	R38	Irritating to the skin
1-methoxy-2-propanol	-	R10	Flammable
1-phenoxy-2-propanol	-	R36	Irritating to the eyes
Glycol ether(s)	1-Methoxy-2-propanol and 2-Methoxy-l-propanol	R36/38	Irritating to the skin and eyes
2-(2-butoxyethoxy) ethanol	-	R36	Irritating to the eyes
2-methoxy-1-methylethyl acetate	-	R10, R36	Flammable, Irritating to the eyes
3-buxtoxypropan-2-ol	-	R36/38	Irritating to the skin and eyes
Gamma-butyrolactone	-	R22, R36/38	Harmful if swallowed, irritating to the skin and eyes
Lauramine Oxide	-	Not available	Not available
Methyl esters	-	Not available	Not available
Mono-isopropylamine	-	R12, R24, R25, R36, R37, R38	Extremely flammable, toxic in contact with skin, toxic if swallowed, irritating to the eyes, irritating to the respiratory system, irritating to the skin
Non-ionic surfactants, Non-ionic tensides	Water soluble soap	R22, R41, R36/38	Harmful if swallowed, risk of serious damage to the eyes, irritating to the skin and eyes
Salt of dodecyl benzene sulphonic acid		R36/38	Irritating to the skin and eyes
Sodium metasulfate	Probably actually sodium metabisulfite	R22-34	Toxic
Tetrasodium salt of ethylenediamine tetraacetic acid	Chelating agent. More commonly known as Ethylene Diamine Tetraacetic Acid Tetrasodium Salt (EDTA)	R22, R36	Harmful if swallowed, irritating to the eyes
Thickeners	Unknown identity	-	-
Water	Diluent	-	Harmless

1.6 AIMS OF THIS WORK

The main aim of this work is to test a range of readily available chemically resistant gloves against actual graffiti removal formulations. The initial phase of this work will involve the screening for unsuitable of gloves against the products. This will be followed by assessment of the gloves resistance to permeation using the continuous contact test method based on the BS EN 374-3 continuous contact permeation test method. Samples of the graffiti removal solutions GC 300, Blitz GS and DSI 6000 were supplied to HSL by the manufacturers at no cost whilst NMP was purchased from Aldrich and Graffiti Gone CR-GR1 was purchased from PACO systems.

1.7 NMP BASED FORMULATIONS USED IN THIS WORK

The ingredients of the formulations NMP based formulations used in this work are listed in Table 1.2. The NMP based formulations GC 300 and DSI 6000 are rather viscous in comparison with NMP. Blitz GS is of a lower viscosity in comparison with NMP and Graffiti Gone CR-GR1 is of a rather similar viscosity to NMP and of the four commercial graffiti removal solvent mixtures used in this work both Blitz GS and Graffiti Gone CR-GR1 contain citrus terpenes.

2 4-HOUR SCREENING EXPERIMENTS

The gloves detailed in Table 2.1 were selected for initial 4-hour screening experiments. They were selected using the criteria of perceived chemical protection. Those gloves that were found to be prohibitively expensive and difficult to obtain were excluded from the study.

Table 2.1 Gloves selected for initial screening experiments

Code	Manufacturer	Description	Single use/ Reusable (S/R)	Material	Thickness (mm)*
A	Kimberly-Clark	Safeskin Purple	S	Nitrile Rubber	0.1 (0.13)
B	Ansell Edmont	Solvex Green	R	Nitrile Rubber	0.28 (0.43)
C	PolyCo	Finesse PF	S	Vinyl (Polyvinylchloride, PVC)	0.14
D	PolyCo	Finity Disposable Stretch Vinyl	S	Vinyl (Polyvinylchloride, PVC)	0.08
E	Arco	Lightweight Latex Pink	R	Latex Rubber	-
F	Arco	Heavyweight Latex Black	R	Latex Rubber	-
G	Ansell Edmont	Industrial (29-845)	R	Neoprene (polychloroprene/ synthetic rubber)	0.43
H	Marigold	Industrial Tripletec Plus G44R	R	Latex Rubber with Nitrile Rubber coating	-
I	Marigold	Z51G Long Nitrosolve	R	Nitrile Rubber	0.28
J	KCl 898	Butoject	R	Butyl Rubber	0.7 (0.69)
K	KCl 897	Butoject NEU	R	Butyl Rubber	0.3
L	KCl 727	Neoprene Nitrile I	R	Neoprene/Nitrile Rubber	-
M	KCl 717	Neoprene Nitril II	R	Neoprene/Nitrile Rubber	0.7
N	Marigold	S340 Medical gloves	S	Latex Rubber	-
O	Ansell Edmont	Conform	S	Latex Rubber	0.13 (0.14)
P	KCl 890	Vitoject	R	Viton	0.7
Q	Mapa	Professional	R	Neoprene (polychloroprene/ synthetic rubber)	0.56
R	SHOWA	660/36 Gauntlets	R	Vinyl (Polyvinylchloride, PVC)	1.5
S	Ansell Edmont	35-405 proFood	S	Polyethylene	0.03 (0.02)
T	North	Silver Shield	S	Layered Polyethylene and ethane-vinyl alcohol	0.07 (0.08)

* Values in brackets were determined in this work

The screening test was a continuous contact test for 4 hours. The experimental set up is pictured in Figure 2.1. Specifically, a number of types of gloves were tested in triplicate against pure NMP and the graffiti removal solutions GC 300 and DSI 6000. Firstly fingers were cut from the gloves. The fingers were turned inside out and each were placed, finger pointing down, into 15 ml capacity glass beakers. 0.25 ml of each solution were added by pipette into the fingers for testing. The fingers were observed for visible breakthrough (BT), discolouration (D) and swelling (SW). BT was defined as visible moisture on the outside of the glove which was detected by the wetting of absorbent material, D covers a multitude of possible changes in glove structure including a recognisable colour change, splitting, melting and other distortions of shape and SW is a recognisable increase in volume or bulging of the sample. The results of these screening tests are shown in Table 2.2.

Figure 2.1 Experimental set up for 4-hour continuous contact screening test featuring: inside-out finger of glove placed upright in a beaker. The test liquid is pippetted carefully into the inside-out finger of the glove

Table 2.2 Results of 4 hour glove screening tests against pure NMP and the graffiti removal solutions GC 300 and DSI 6000

Glove reference code	**NMP**			**GC 300**			**DSI 6000 GR**		
A	BT	BT	BT	D	D	D	D	D	D
B	SW	SW	SW	SW	SW	X	D	D	D
C	BT	BT	BT	BT	BT	BT	SW	SW	SW
D	BT	BT	BT	BT	BT	BT	BT	BT	BT
E	BT	BT	BT	X	X	X	X	X	X
F	X	X	X	X	X	X	X	X	X
G	Void	BT	BT	X	X	X	X	X	X
H	BT	BT	BT	X	X	X	X	X	X
I	BT	BT	BT	X	X	X	X	SW	SW
J	X	X	X	D	D	D	D	D	D
K	X	X	X	X	X	X	X	X	X
L	X	X	X	X	X	X	X	X	X
M	BT	BT	BT	X	X	X	X	X	X
N	SW BT	SW BT	SW BT	SW	X	X	X	X	X
O	BT	BT	BT	BT	BT	BT	BT	BT	BT
P	X	X	X	X	X	X	X	X	X
Q	X	X	X	X	X	X	X	X	X
R	D	D	D	X	X	X	X	X	X
S	X	X	X	X	X	X	X	X	X
T	X	X	X	X	X	X	X	X	X
X = no visible effect , BT = breakthrough, D = discolouration and SW = swelling									

Of the 20 glove types that were tested, 7 glove types showed no visible degradation following four hours continuous contact with each of the 3 solvent solutions. These were gloves F, K, L, P, Q, S and T (see Table 2.1 for explanation of glove codes and Table 2.2 for results). Those exhibiting BT, SW or both are clearly unsuitable for prolonged contact with the solvents that they were tested against. Degradation may not be an indication of BT, but it is indicative of superficial solvent-glove interaction, which may lead to failure. Apart from glove type S, those gloves that are thin and commonly regarded as disposable were, perhaps understandably, particularly prone to failure by BT.

Generalising, pure NMP appeared to be much more aggressive to the glove material than both GC 300 and DSI 6000 GR formulations.

3 SWELLING TESTS

3.1 INTRODUCTION TO SWELLING TESTS

Swelling tests were performed on samples cut from a series of glove types. Swelling tests are a common method of assessing the extent of cross-linking in man-made polymers. Rather than dissolving completely a cross-linked polymer, the polymer will absorb the solvent and subsequently swell. Polymers swell until they reach a thermodynamic steady state, at which time the elastic forces of the cross-links curtail the elongation of individual polymer chains by the solvation process. Researchers measure swelling by gravimetric methods, as discussed in ASTM D2765-95. The most commonly quoted value is the swell ratio of a cross-linked polymer (see Equation 3.1). Once this value is known the extent of cross-linking of the polymer may be calculated.

$$q = \frac{Wd + (Wg - Wd)\,K}{Wd}$$

Wg = mass after, Wd = mass before, q = swelling ratio, K = the ratio of the densities of the solvent to the polymer

Equation 3.1 Swell ratio of a cross-linked polymer

While the extent of cross-linking of a glove may be of little interest to the occupational hygienist –the uptake of solvent into the glove is relevant. The 4-hour screening experiments showed that some gloves exhibited swelling. In the case of samples of the reusable nitrile glove type B, swelling occurred prior to any evidence of breakthrough. It is for this reason that the swelling of some glove types to NMP and some graffiti removal products were investigated. In addition, it was thought that results from the gravimetric method of measuring solvent uptake by gloves might be directly related to the breakthrough time. Given that the gravimetric method of measuring solvent uptake is rather simple to accomplish, it may be that this method could be a cheap screening test to use prior to glove breakthrough tests [30], which require a capital investment in equipment in the order of £10K. An alternative method is performed by the German glove manufacturer KCL who measure the diameter of a circular sample of glove material before and after exposure to a chemical. The author considers the gravimetric method to be superior because the availability of high accuracy balances facilitates greater accuracy.

3.2 EXPERIMENTAL PROCEDURE OF SWELLING TEST

The experimental set up for the swelling tests is pictured in Figure 3.1. Circles of glove material to be tested were cut from the palm or back of the glove. These were each cut to measure 22 mm in diameter, were inscribed with an identification number and were weighed to the nearest 0.1 mg. The mass of each circle of glove material was recorded (Wd). The circles were used as gaskets to fit between the lid and the mouth of a sample tube containing either NMP or a graffiti removal solution. Upon inversion of the sample tube the glove material ‘gasket’ would be exposed to the solvent challenge. At the end of each test each sample tube was up-righted. The ‘gasket’ was removed and dabbed dry of extraneous solvent residing on its surface. Finally the mass of the ‘gasket’ was recorded (Wg). Wg minus Wd equals the mass of solvent uptake. By preparing a series of pre-weighed samples or the same glove type it was possible to record solvent uptake by mass at a series of time intervals. In this work measurements were commonly made at 8 hrs, 24 hrs and at intervals between 0 and 8 hrs.

This experiment differs from ASTM D2765-95 in that in this test only one side of the glove material is exposed to the solvent in order to mimic actual glove use. A similar test has been reported by Roff et al. [31]

Figure 3.1 Experimental set up for the swelling tests featuring (left-to-right) glove material gasket; lid; bottle containing test liquid and assembled test

3.3 RESULTS AND DISCUSSION OF SWELLING RESULTS

Figures 2-14 display plots of the results from the degradation tests that were conducted on glove types A, B, E, F, G, H, J, L, M, N, S and T using NMP, GC 300, DSI 6000, Blitz GS and Graffiti Gone CR-GR1. The raw data is tabulated in the appendix: Table 6.1 to Table 6.12. Examination of the data shows that the degree of solvent uptake was heavily dependant upon both the solvent identity and glove type. Therefore, overall trends in the results are difficult to elucidate. The two factors are roughly separated in the following discussion:

3.3.1 Solvent identity

Pure NMP was often the more aggressive solvent of those tested against glove samples. Of the four graffiti removal formulations Blitz GS was generally the more aggressive solvent. Blitz GS is even more aggressive than pure NMP against glove types E, F, J and L. This is an indication that D-Limonene, present as a coformulant with in Blitz GS, is either a very aggressive solvent in itself or acts as a solvent in synergy with NMP.

Generalising, the GC 300, DSI 6000 and Graffiti Gone CR-GR1 graffiti removal solutions were frequently absorbed by gloves to a similar degree, and in the case of some glove types rather differently than were NMP and Blitz GS. However, Figure 3.2 shows that DSI 6000 behaved rather differently to GC 300 in the case of glove A, even though their formulations are appreciably similar. This latter observation illustrates the unpredictability of glove permeation rather well.

3.3.2 Glove type

Glove types S, T and J could be described as offering good resistance to NMP. These gloves also resisted permeation by GC 300, DSI 6000 and Graffiti Gone CR-GR1. However, glove J was attacked by Blitz GS quite readily. The low uptake of solvent by glove types S and T is probably because of the difference in polarity between NMP and the polyethylene glove material. When polarities are opposed things repel. NMP is a very polar solvent and polyethylene is non-polar because it is formed from only carbon and hydrogen atoms. The low solvent uptake of S is particularly surprising given that the glove type is not marketed as chemically resistant and it is made from very thin material.

Latex glove types E and F were found to give moderate resistance to uptake of NMP, GC 300, DSI 6000 and Graffiti Gone CR-GR1.

'A' type gloves were most notable for their poor NMP resistance: samples expanded in the presence of the solvents and often ruptured upon removal from the test rig. Particularly poor were the nitrile gloves (A and B), which swelled enormously (see Figure 3.14 for a picture of a swollen sample of glove type B owing to uptake of NMP and less so to GC 300, Graffiti Gone CR-GR1 and DSI 60000). Those gloves containing nitrile rubber as a co-ingredient (L & M) also performed poorly against both the NMP and the formulations. Certainly, these gloves should not be used, even for short tasks, in the proximity of NMP or NMP based formulations. It is particularly concerning that nitrile and nitrile containing gloves samples take up NMP and then 'sweat' it back out again over time (an example of a sweating glove sample is pictured Figure 3.14).

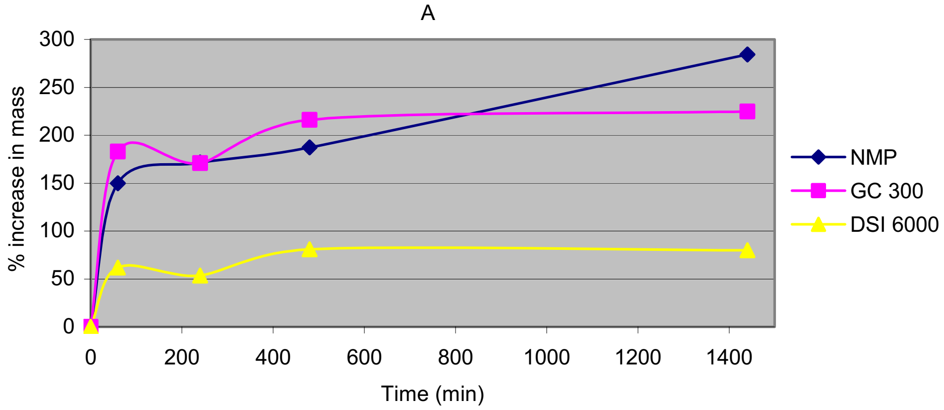

Figure 3.2 Swelling data for Kimberly-Clark Safeskin Purple single use (A)

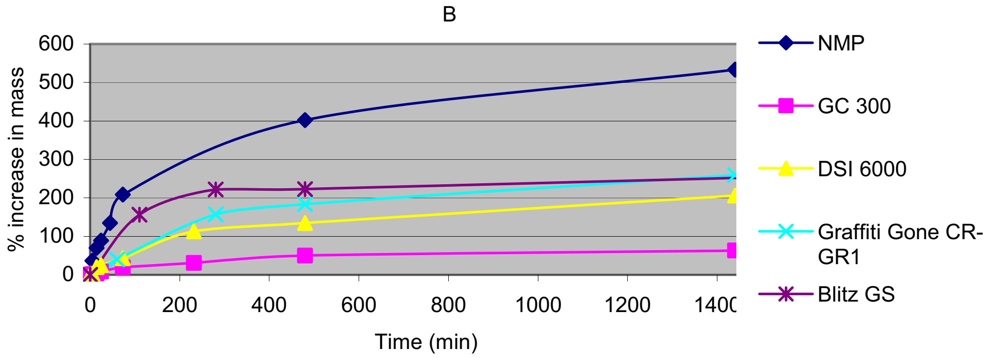

Figure 3.3 Swelling data for Ansell Edmont Solvex Nitrile Reusable (B)

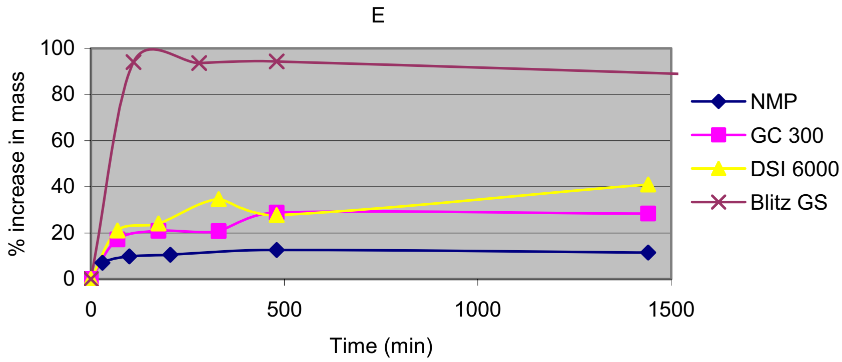

Figure 3.4 Swelling data for Arco Lightweight G01R Pink Latex (E)

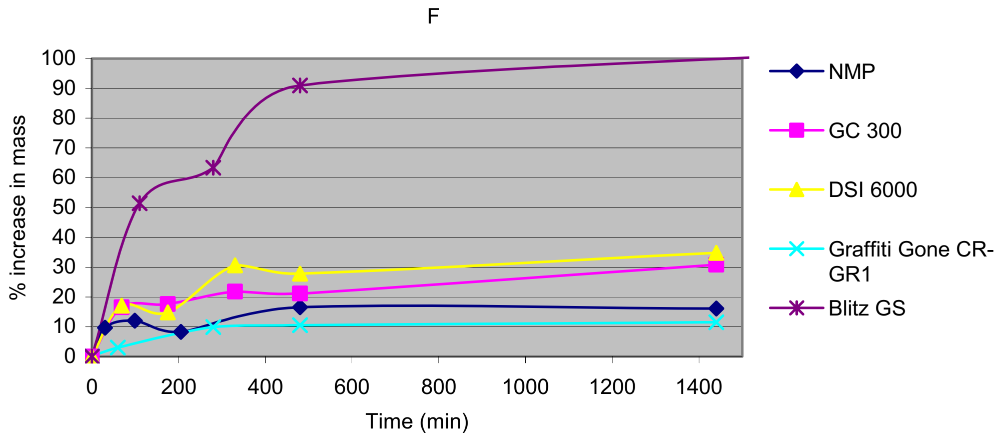

Figure 3.5 Swelling data for Arco Heavyweight Black Latex (F)

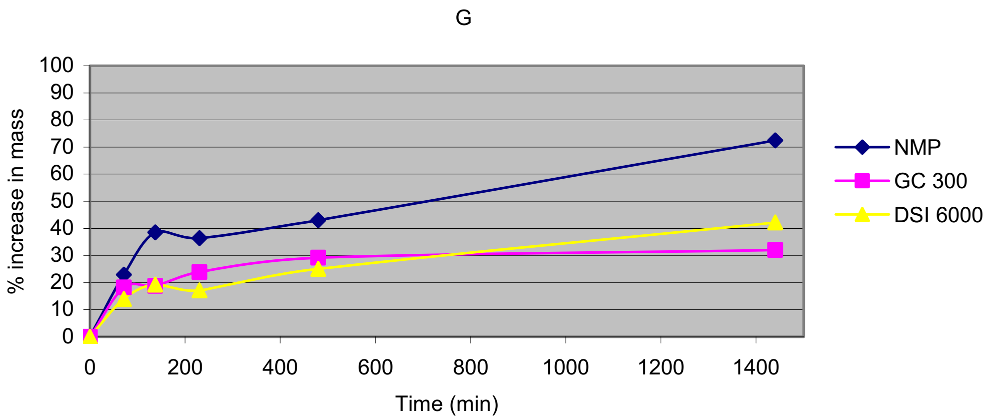

Figure 3.6 Swelling data for Ansell Edmont Industrial Neoprene (G)

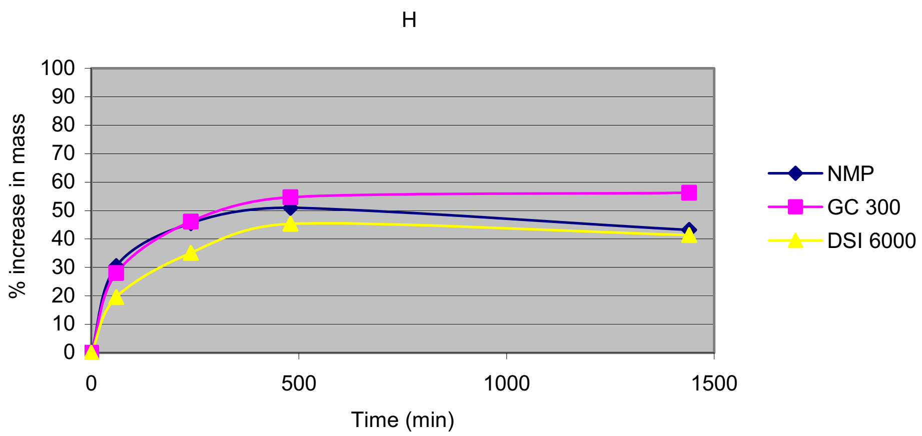

Figure 3.7 Swelling data for Marigold Tripletec Plus G44R Industrial Red Latex (H)

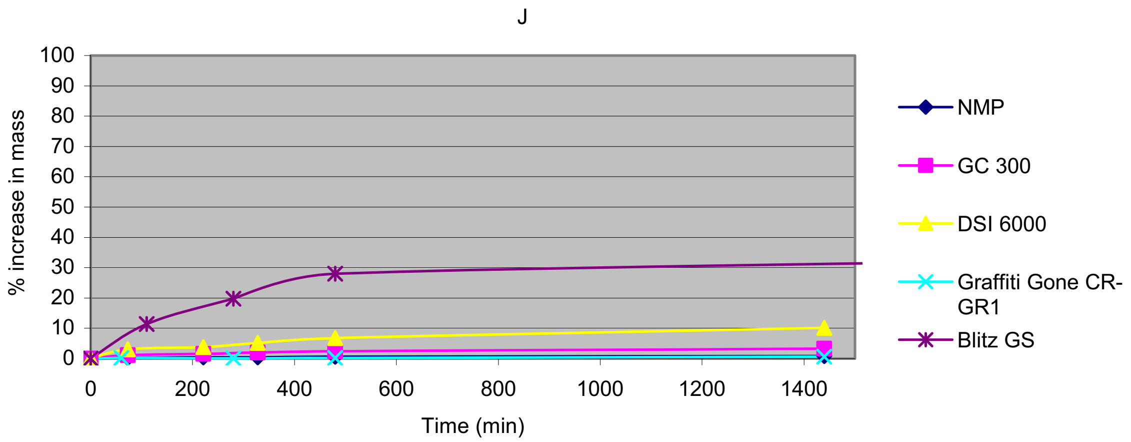

Figure 3.8 Swelling data for KCL 898 Butoject (J)

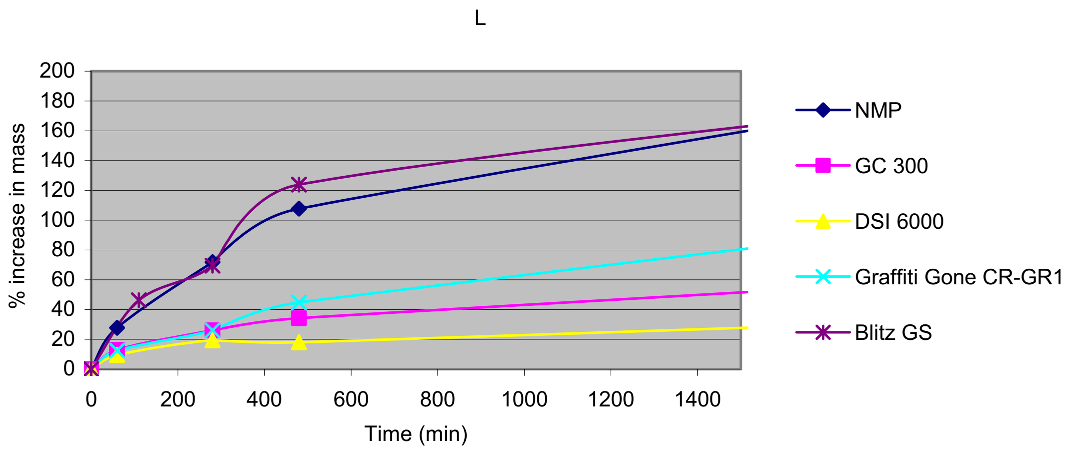

Figure 3.9 Swelling data for KCL 727 Nitopren (L)

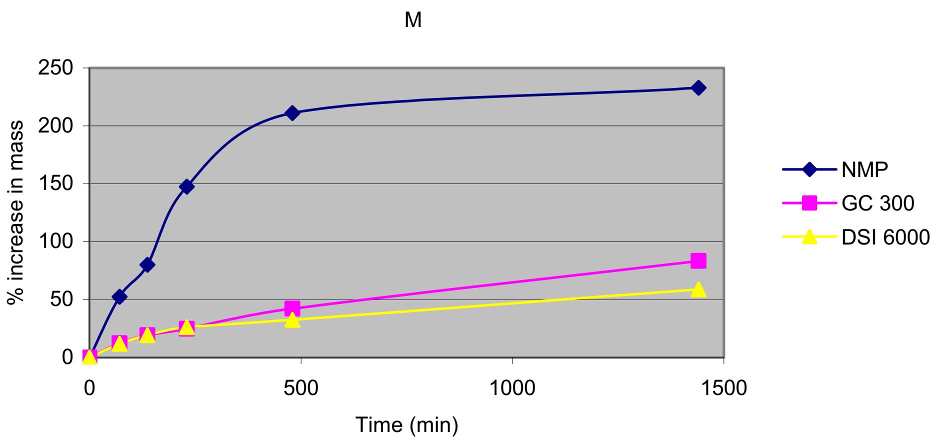

Figure 3.10 Swelling data for KCL 717 Nitopren (M)

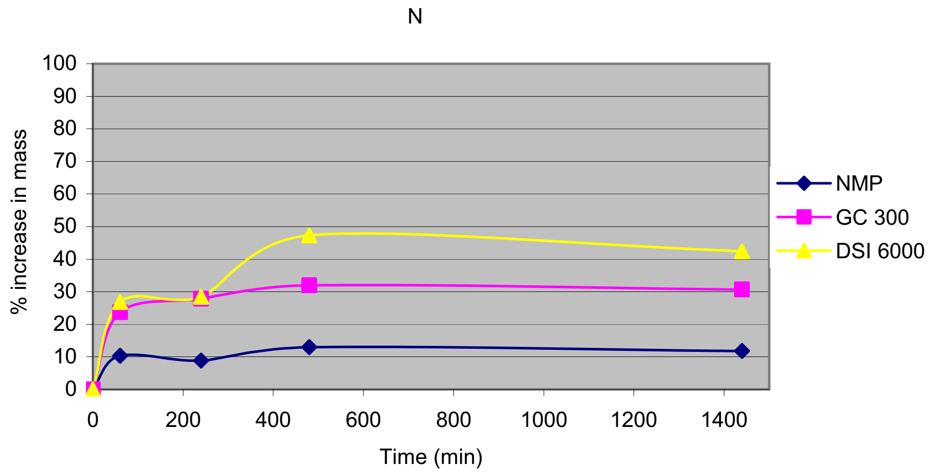

Figure 3.11 Swelling data for Marigold Medical S340 (N)

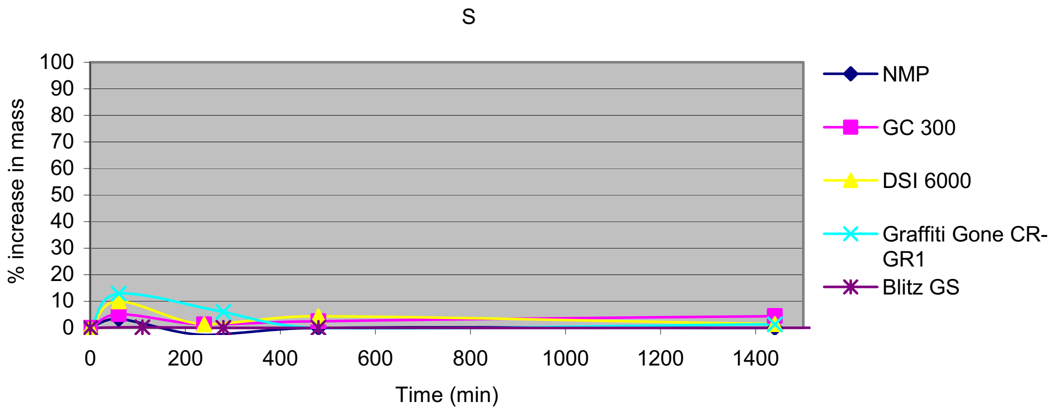

Figure 3.12 Swelling data for Ansell Edmont 35-405 proFood (S)

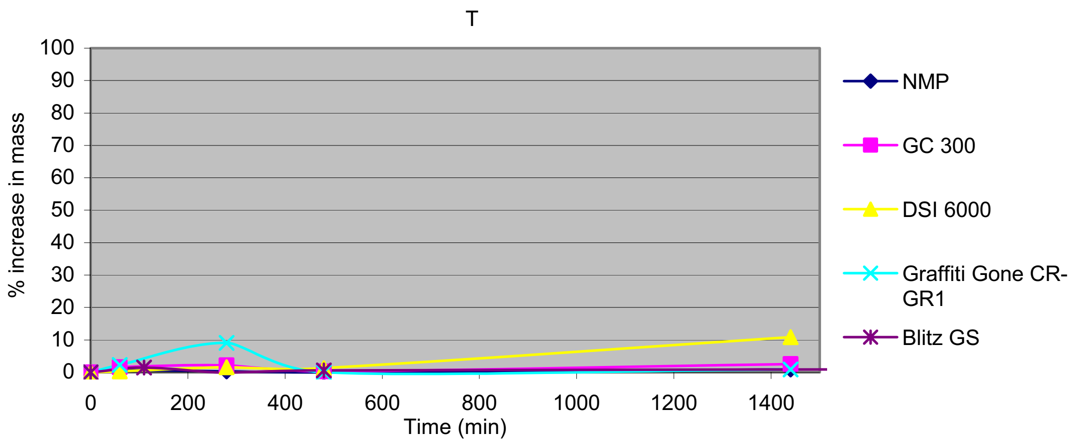

Figure 3.13 Swelling data for North Silver Shield (T)

Figure 3.14 Solvent-swollen reusable Solvex nitrile glove material (B), pictured after 8 hrs of continuous contact with (left to right) NMP, GC300, DSI 6000 and no solvent. The NMP swollen sample is surrounded by solvent that it has sweated out following its removal from the test rig

3.4 DISCUSSION OF SWELLING RESULTS AT 8 HOUR POINT

Given the importance attached to measurements of full shift 8 hr exposures it is worth examining the swelling results at this point. The 8 hour period in these experiments also has the advantage of being a point at which the behaviour of each type of glove with a solvent will have diverged, thus allowing clear analysis. The measurements made after 8 hrs are displayed in Figure 3.15 grouped by solvent formulation type. In comparison with KCL's swelling assessment criteria [31][1], detailed in Table 3.1, only two glove types could be classed as resistant to NMP and NMP based formulations, these are S & T. Glove J is resistant to all liquids it was tested against apart from Blitz GS. Patterns within these swelling results are relatively hard to identify. In Figure 3.16 the same data is grouped by glove material type. Examination of this plot reveals that the glove material is the major determining factor of swelling increase rather than the solvent formulation type. Those gloves containing nitrile rubber (A, B, L & M) are clearly unsuitable for use with these NMP based solvent formulations, having particularly high penetration by NMP. The latex rubber type gloves offer greater solvent swelling resistance; two of the four latex glove type tested in this manner were found to offer partial resistance to NMP swelling by KCL's criteria, these were E & N. The latex glove F showed partial resistance only to GC300. The neoprene glove E, was no better than the latex types.

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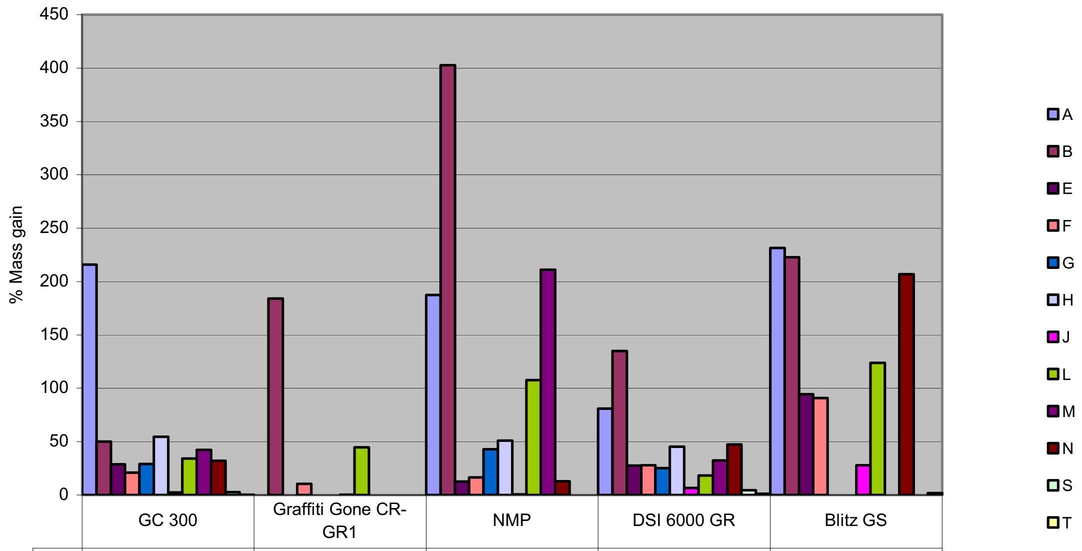
[1] *Kächele-Cama Latex GmbH, Industriepark Rhön , Am Kreuzacker 9, D-36124 Eichenzell, Telephone: ++49 (0) 6659 - 87 300, Fax: ++49 (0) 6659 - 87 155, E-Mail: sales@kcl.de Homepage: www.kcl.de*



	GC 300	Graffiti Gone CR-GR1	NMP	DSI 6000 GR	Blitz GS
A	216.0		187.3	80.9	231.5
B	50.2	184.0	402.5	135.0	222.9
E	28.8		12.7	27.7	94.3
F	21.1	10.5	16.5	27.8	91.0
G	29.2		43.0	25.1	
H	54.7		50.9	45.3	
J	2.4	0.2	0.6	6.7	28.0
L	34.2	44.8	107.7	18.2	123.9
M	42.3		211.0	32.5	
N	32.0		13.0	47.3	206.7
S	2.6	0.0	0.0	4.3	0.0
T	0.3	0.0	0.0	1.3	1.9

Figure 3.15 Percentage mass gain of samples of glove in contact with NMP, GC 300, DSI 6000, Graffiti Gone CR-GR1 and Blitz GS solvents following 8 hours of exposure. Grouped by solvent

Table 3.1 KCL's swelling assessment criteria and a tally of the number of gloves that were swell tested in this work that fall into each degradation group. The original data is in Figure 3.15

Degradation (swelling %) within 8 hrs	**Assessment by KCL**	**NMP**	**Blitz GS**	**GC300**	**DSI 6000**	**Graffiti Gone CR-GR1**	**All**
< 6.8	+ (resistant)	3	2	3	3	3	2
>6.8 >15.0	O (partially resistant)	5	0	0	0	1	1
>15.0	- (non-resistant)	4	7	9	9	2	9
	Totals	12	9	12	12	6	12

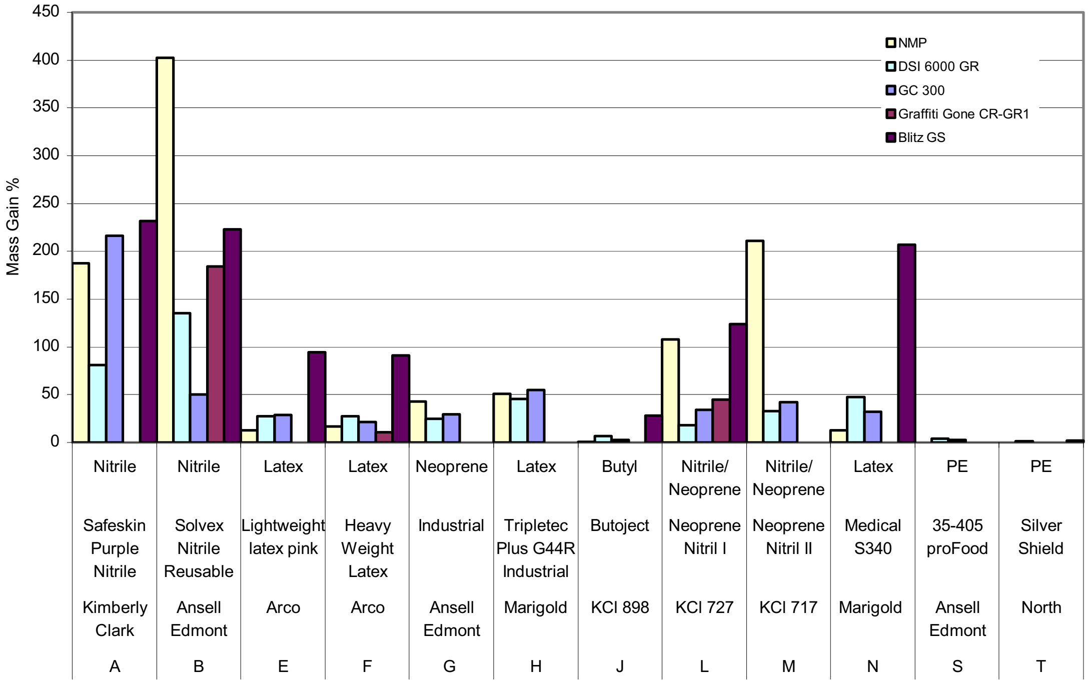


Figure 3.16 Percentage mass gain of samples of glove in contact with NMP, GC 300, DSI 6000, Graffiti Gone CR-GR1 solvents following 8 hours of exposure. Grouped by glove material

It is now possible to attempt to make some conclusions about whether it would have been possible to make correct glove choices for use with the formulations based on only pure NMP swelling data:

Figure 3.17 is a plot of the glove sample mass gain by NMP of each glove type that was measured. The positive and negative T-bars illustrate the range of % mass gain that was measured for the formulations, an indication of the potential for error of judgement of sorts. In selecting gloves for use with a NMP based formulation a bad situation would be to make a glove choice based on pure NMP, that was not only false, but that the formulation was actually much more aggressive to the glove than NMP. Figure 3.17 shows that the likelihood of this occurring is high given that the NMP containing formulations were significantly more penetrative to 6 glove types than was pure NMP. Therefore, it is not recommended that chemically protective glove selection be based on permeation testing results obtained using model compounds, simplified formulations or single ingredients as in this type of test.

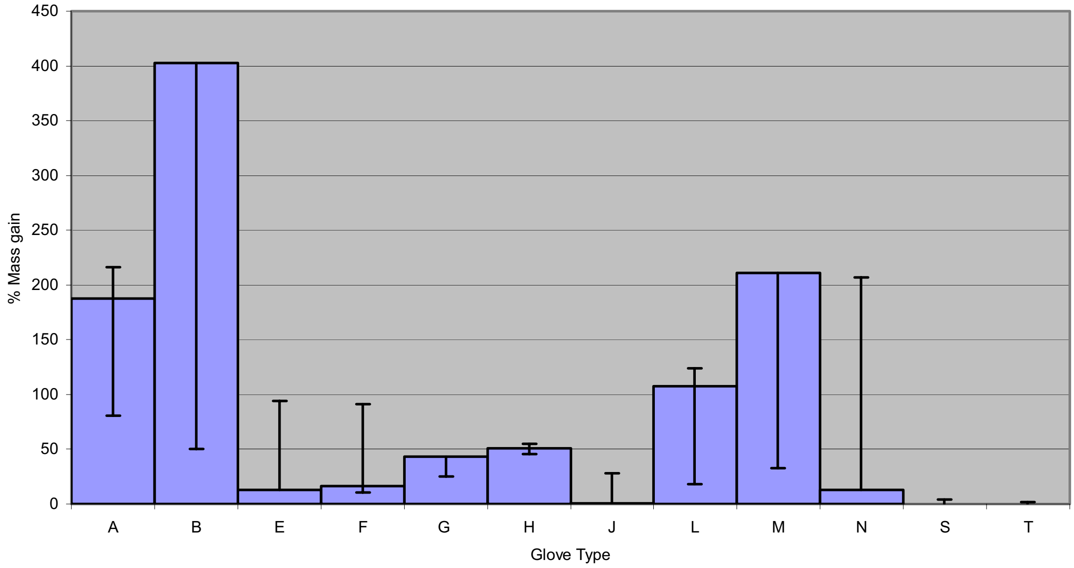


Figure 3.17 Plot of glove sample mass gain due to NMP swelling after 8 hours (blue). The positive and negative T-bars illustrate the range of % mass gain that was measured for the NMP formulations after 8 hours

4 GLOVE PERMEATION TESTS

4.1 GLOVE AND TEST SELECTION

A subset of the glove types was selected for permeation testing. Latex disposable (e.g. N or O), nitrile disposable gloves (e.g. A), and reusable nitrile gloves (e.g., B) were selected because their use by actual graffiti removers has been recorded [1]. The screening tests have indicated that these gloves do not offer good resistance to NMP or the NMP containing formulations. In addition, three of the seven glove types that showed no breakthrough, discolouration or swelling in the four-hour screening tests were selected for testing, these were J, S and T. Only one KCL glove type was tested further (J) because their products have been already been tested thoroughly against pure NMP and because they are not easily available in the UK.

4.2 METHOD

4.2.1 Chemical permeation

Chemical permeation tests were performed (in triplicate) following method BS EN 374-3 (BSI 2003a).[30] Samples of six glove types (A, B, J, O, S and T) were tested against NMP. Permeation was measured using a flame ionisation detector (FID) to detect volatile organic compounds (VOCs) permeating through the glove. The FID (Signal 3000HM) was calibrated with methane, however because sensitivity changes with VOC type the data collected was adjusted retrospectively.

The three best performing gloves North Silver Shield (T), KCL Butoject (J) and Ansell ProFood (S), were then tested further against Graffiti Gone CR-GR1, a graffiti removal formulation containing NMP. Graffiti Gone CR-GR1 was selected because the authors were able to obtain a large sample of the solution at low cost. Samples were taken of the permeant vapour and this was analysed by gas chromatography in order to determine the composition of the vapour for retrospective calibration of the FID.

Glove thickness measurements were taken of the samples as part of the test. A Sylvac digital comparator was used that exerts 22.5 kPa pressure on the test piece via a 5 mm diameter flat anvil.

4.2.2 Chemical degradation

A number of further tests were performed in order to determine whether the glove material had been affected by contact with the test materials. The appearance of samples before and after the test were observed, and the samples were weighed before and after the permeation test to determine if there had been any mass change due to either swelling or solvation. The glove was dried with a paper towel as much as possible before it was reweighed, however, this was difficult for samples that had stretched out of shape. The exposed glove samples also underwent a puncture resistance test to see if the mechanical strength of the sample had been altered.

Glove puncture resistance testing was performed using a Testometric CX materials testing machine following a method based upon BS EN 388 (BSI 2003b) [32], but having no preliminary standard conditioning period. Puncture testing was carried out immediately after termination of the permeation test (8 h of continuous contact). For comparison, six samples of each glove type were also puncture tested without having undergone the chemical permeation test. These samples were preconditioned for temperature and humidity. Although EN 388 requires the test to be performed on only four samples, in this work six samples were tested to improve the statistical significance of the results.

4.3 RESULTS

4.3.1 Chemical permeation and degradation tests

The results are summarised in Table 4.1, and fully tabulated in Table 4.2 and Table 4.3. The results can also be expressed using the "performance level" classification system described in the respective standards and employed by the glove industry. These are both defined in Table 4.4. In line with the respective standards, the lowest values recorded were used to determine performance levels.

4.4 OBSERVATIONS

The observations that were made during the glove testing against pure NMP are summarised below:

- Kimberly-Clark Safeskin (A)
  Sample weakened and stretched by pressure of fluid and tore easily on handling. Massive weight increase due to swelling (see Table 4.1).

- Ansell Solvex (B)
  Sample weakened and stretched. Massive weight increase due to swelling (see Table 4.1).

- Ansell ProFood (S)
  No sign of degradation.

- North Silver Shield (T)
  No sign of degradation

- KCL Butoject 898 (J)
  No sign of degradation.

- Ansell Conform+ (O)
  No signs of degradation, however a small weight increase due to swelling (see Table 4.1).

4.5 DISCUSSION

The disposable 'single use' gloves (Kimberly-Clark Safeskin (A), Ansell Conform+ (O) and Ansell ProFood (S)) allowed NMP to permeate very quickly and did not even reach level 1 permeation resistance. Although the thicker Ansell Solvex nitrile gloves (B) did resist permeation for greater than 10 minutes, they in common with the thin A gloves underwent degradation, stretching and tearing easily. North Silver Shield (T) and KCL Butoject 898 (J) performed well over the 8 h test period. Although S allowed permeation after a short period, and the permeation rate passed the 1 $\mu g.cm^{-2}.min^{-1}$ rate used for determining the normalised breakthrough time, the permeation rate was still relatively low. Consequently the J, S and T gloves underwent further testing with the Graffiti Gone formulation.

In testing against Graffiti Gone CR-GR1, J and T again resisted permeation very well. S gloves again allowed permeation very quickly, and the permeation rate appears to be marginally higher than when tested against NMP, however the material passing through the glove was now a mixture comprising mostly of NMP and limonene (in roughly equal proportions), with traces of 2-(2-butoxyethoxy) ethanol, dimethyl glutarate and dimethyl succinate. These gloves are exceptionally thin, and a thicker version would have reduced the permeation rate.

There were no visible signs of degradation of glove types J, S and T in tests against Graffiti Gone CR-GR1, nor did the weight change and puncture resistance tests reveal any changes. Due to the limited number of samples tested the level of accuracy for the puncture resistance test is lower than might be desirable, however comparison of the data sets shows that there was very little difference in glove performance between exposed and unexposed gloves. It should be mentioned that the S and T gloves are not as robust as the J gloves. In practice they could be combined with another glove type to protect them from physical damage.

4.6 CONCLUSION

The best performing gloves tested were the North Silver Shield (T) and KCL Butoject gloves (J), which resisted continuous contact permeation for over eight hours when tested against NMP and a commercial cleaning formulation (Graffiti Gone CR-GR1).

Nitrile gloves (A and B) are unsuitable for use with NMP due to rapid degradation allowing a high permeation rate, and leaving them weakened.

Thin latex gloves (O) were also unsuitable for use with NMP due to very short breakthrough times and a high permeation rate.

Polyethylene gloves (S) also had short breakthrough times but allowed only a relatively low permeation rate.

Table 4.1 Summary Results

Criterion	Kimberly-Clark Safeskin 52002M (A)	Ansell Conform+ 69-150 (O)	Ansell Solvex 37-675 (B)	Ansell ProFood 35-405 (S)	KCL Butoject 898 (J)	North Silver Shield (T)
Material	Nitrile	Latex	Nitrile	Polyethylene	Butyl	Laminate‡
Thickness (mm)	0.13	0.14	0.43	0.02 n=6	0.69 n=6	0.08 n=6
Weight/unit area (g/m²)	120	129	402	16 n=6	795 n=6	78 n=6
NMP						
Normalised Breakthrough Time (min)	~2*	~2	21†	~3	>480	>480
Performance Level	0*	0	1†	0	6	6
Steady State Permeation (µg/cm²/min)	>34*	>26	32†	1.2	<0.1	~0.1
Weight Change (%)	>+300	+8	+155	+0.7	+0.2	+0.9
Graffiti Gone CR-GR1						
Normalised Breakthrough Time (min)	-	-	-	~2	>480	>480
Performance Level	-	-	-	0	6	6
Steady State Permeation (µg/cm²/min)	-	-	-	1.6	<0.1	<0.1
Weight Change (%)	-	-	-	+2.8	0.0	+0.3
Standard Puncture Test (N)	-	-	-	0.91 n=6	23.48 n=6	5.35 n=6
Performance Level	-	-	-	0	1	0
Degradation Puncture Test (N)	-	-	-	1.00	23.67	5.71

- No test performed
* Glove underwent acute chemical degradation resulting in distension and splitting of the material.
† Glove became distended and tore during removal after the test.
‡ Laminate of polyethylene and ethylene vinyl alcohol.

Notes

Results summarised from tests in triplicate except where noted.
Thickness and weight/unit area are means.
Breakthrough times and Puncture Test results are minimums.
Steady state permeation and weight changes are medians.
Performance level as per relevant standard (Table 4.4).

Table 4.2 Permeation test results

Sample / Chemical	Median Thickness (mm)	Weight (g)	Breakthrough Time (mins)	Permeation Rate (max) (µg.cm⁻².min)	Weight Increase (%)
Kimberly-Clark Safeskin 52002M (A) versus NMP					
1	0.13	0.544	~3*	-*	-
2	0.12	0.516	~2	>35	>+300
3	0.13	0.568	~3	>34	>+300
Ansell Conform+ (O), 69-150 versus NMP					
1	0.14	0.563	~2	26	+7
2	0.15	0.584	~4	24	+8
3	0.14	0.585	~3	>26	+10
Ansell Solvex (B), 37-675 versus NMP					
1	0.40	1.646	21*	32*	>+300
2	0.44	1.961	41	27	+110
3	0.43	1.821	32	32	+155
Ansell ProFood 35-405 (S) versus NMP					
1	0.02	0.074	19	1.2	+0.7
2	0.02	0.069	7	1.1	+0.7
3	0.02	0.070	~3	1.6	+1.6
North Silver Shield (T) versus NMP					
1	0.08	0.342	>480	~0.1	+0.9
2	0.09	0.367	>480	<0.1	+0.8
3	0.08	0.351	>480	<0.1	+2.0
KCL Butoject 898 (J) versus NMP					
1	0.76	3.706	>480	<0.1	+0.2
2	0.65	3.286	>480	<0.1	+0.1
3	0.65	3.315	>480	<0.1	+0.2
Ansell ProFood 35-405 (S) versus Graffiti Gone CR-GR1					
1	0.01	0.064	~2	2.0	+3.3
2	0.02	0.073	~4	2.9†	+4.4†
3	0.02	0.068	~4	1.6	+2.8
4	0.02	0.073	~4	1.6	+1.8
North Silver Shield (T) versus Graffiti Gone CR-GR1					
1	0.09	0.349	>480	<0.1	+0.3
2	0.08	0.324	>480	<0.1	+0.6
3	0.08	0.342	>480	<0.1	+0.3
KCL Butoject 898 (J) versus Graffiti Gone CR-GR1					
1	0.692	3.476	>480	<0.1	0.0
2	0.742	3.750	>480	<0.1	-0.1
3	0.712	3.560	>480	<0.1	0.0

Note

Breakthrough times are to 1 $\mu g.cm^{-2}.min^{-1}$ as per EN 734-3.
Permeation Rate is the maximum rate recorded over the test period, and is not necessarily a steady state permeation rate.
* Glove underwent acute chemical degradation resulting in distension and splitting of the material during the test.
† Sample damaged during test

Table 4.3 Puncture test results			
Test Conditions	**Puncture Resistance (in Newtons) by Glove Type**		
	Ansell ProFood 35-405 (S)	KCL Butoject 898 (J)	North Silver Shield (T)
Standard BS EN 388 Test	0.91 0.92 0.96 1.05 1.14 1.37	23.48 23.53 23.67 23.80 23.89 25.67	5.35 6.37 6.74 6.89 7.10 7.29
Test after 8 h exposure to Graffiti Gone CR-GR1	1.00 1.06 1.11 1.11*	23.67 24.75 24.51	5.71 6.48 6.93
* Sample damaged during test			

Table 4.4 Performance level requirements

Permeation Resistance		**Puncture Resistance**	
Breakthrough Time (min)	**Performance Level**	**Force (N)**	**Performance Level**
>10	1	20	1
>30	2	60	2
>60	3	100	3
>120	4	150	4
>240	5		
>480	6		
Although no performance level of 0 has been defined, it has been used in Table 7 to indicate that the glove failed to meet the lowest requirement of the relevant standard i.e. <10 min for permeation resistance or <20 N for puncture resistance.			

5 CONCLUSIONS

This work has demonstrated that testing of gloves against NMP formulations rather than just neat NMP is necessary. Assumptions of glove choice based on the use of model compounds or similar formulations should be made with extreme caution. There are considerable implications for other industries where aggressive solvents are used as part of formulations. For example, NMP itself appears under a number of trade names including Pharmosolve™ when it is used to solublise drugs. This work has shown that that the disposable latex and single use nitrile gloves used in the medical profession are not suitable to handling drug formulations containing NMP. In the field of Biocides it is vital that co-formulants with actives are properly labelled even when they are deemed 'inert'.[33] This is because all ingredients of mixtures affect glove permeation. Also, it is worth noting that NMP use may be on the increase because it is biodegradable and therefore is perceived as being an environmentally friendly solvent. For example, a recent document produced for the Department for Environment, Food and Rural Affairs (DEFRA) advocates NMP as an alternative paint stripping solvent to dichloromethane (DCM). [34]

The authors have demonstrated the chemical durability of the North Silver Shield glove against NMP and the NMP based formulations GC 300, DSI 6000, Blitz GS and Graffiti Gone CR-GR1. Unfortunately these gloves can be awkward to work in; therefore Butyl rubber gloves may be a preferred choice of a worker. The butyl rubber glove type examined in this work (KCL Butoject 898) had good resistance to NMP, GC 300, DSI 6000 and Graffiti Gone CR-GR1 but not to Blitz GS, an appreciably more aggressive product that is designed to solvate metallic paints but having ingredients in common with most other graffiti removal products. Of the other glove types tested the Latex gloves demonstrated some potential chemical resistance in swelling tests against NMP but less resistance to the NMP containing formulations. It is possible that further testing could establish these gloves suitable as 'splash resistant' and if used should be replaced on a task-by-task basis and immediately when contaminated.

Earlier in this document it was hypothesised that the 4-hour screening and swelling tests conducted in this work may be a cheap way of assessing gloves in less well equipped laboratories. This has been demonstrated in part, however the thin Ansell ProFood (S) glove passed both of these tests and failed the BS EN 374-3 continuous contact permeation test. Therefore, it is only possible to say that the 4-hour screening and the swelling tests are useful guideline and 'look see' tests that could preclude some glove types from further testing or could even be carried out by inspectors shortly after a visit to a site that was using chemicals with unsuitable gloves. This work has proved the two screening tests to be very powerful; in this work the screening tests eliminated 17 glove types from further investigation (although three of the eliminated 17 were permeation tested for other reasons). The 4-hour screening tests eliminated 12 or these 17 glove types from further investigation.

It is worth noting that it would be simple for inspectors and field scientists to carry out the 4-hour screening test in the field. This could is done by obtaining one of the gloves being used on site, turning the finger of a glove inside out and pipetting some of chemical being used on site into it. A handy way of visualising the permeating chemical is to use permeatec pads, which turn black when in contact with a solvent, or to put some blue roll in contact with the 'dry' side of the glove, when the chemical permeates it dampens and it turns the piece of blue roll dark blue.

6 APPENDIX: SWELLING DATA

Table 6.1 Swelling data for Kimberly-Clark Safeskin Purple single use (A)

Kimberly-Clark Safeskin Purple single use (A)								
NMP			GC 300			DSI 6000		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0
147	60	149.8	148	60	183.1	149	60	61.8
144	240	171.5	145	240	170.8	146	240	53.5
139	480	187.3	141	480	216.0	143	480	80.9
138	1440	284.4	140	1440	224.7	142	1440	79.9

Table 6.2 Swelling data for Ansell Edmont Solvex Nitrile Reusable (B)

Ansell Edmont Solvex Nitrile Reusable (B)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
1	5	55.6	7	5	2.1	13	5	2.7	19	60	39.8	26	110	156.1
2	14	99.6	8	14	3.1	14	14	19.9	20	280	157.4	25	280	221.5
3	24	130.7	9	24	8.5	15	24	24.8	21	480	184.0	24	480	222.9
4	44	199.8	10	73	19.3	16	73	43.6	22	1440	259.0	23	2880	296.9
5	73	330.4	11	232	30.9	17	232	113.1						
6	480	577.6	12	480	50.2	18	480	135.0						
40	1440	931.1	41	1440	63.3	39	1440	206.0						

Table 6.3 Swelling data for Arco Lightweight G01R Pink Latex (E)

Arco Lightweight G01R Pink Latex (E)											
NMP			GC 300			DSI 6000			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
76	30	7.0	81	69	17.2	86	69	21.0	87	110	94.0
75	99	9.9	80	175	20.8	85	175	24.0	79	280	93.6
74	205	10.6	89	330	20.7	84	330	34.6	72	480	94.3
73	480	12.7	78	480	28.8	83	480	27.7	243	2880	81.5
88	1440	11.4	77	1440	28.4	82	1440	41.0			

Table 6.4 Swelling data for Arco Heavyweight Black Latex (F)

Arco Heavyweight Black Latex (F)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
49	21.2	30	54	69	16.6	59	69	17.1	60	60	3.0	67	110	51.4
48	27.1	99	53	175	17.6	58	175	14.8	61	280	9.9	66	280	63.3
47	18.3	205	52	330	21.8	57	330	30.6	62	480	10.5	69	480	91.0
46	37.7	480	51	480	21.1	56	480	27.8	63	1440	11.5	45	2880	108.9
45	35.2	1440	50	1440	30.8	55	1440	34.8						

Table 6.5 Swelling data for Ansell Edmont Industrial Neoprene (G)

Ansell Edmont Industrial Neoprene (G)								
NMP			GC 300			DSI 6000		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0
93	71	22.9	99	71	18.2	106	71	13.9
105	137	38.6	98	137	18.8	103	137	19.2
92	230	36.5	97	230	23.9	102	230	17.1
91	480	43.0	96	480	29.2	101	480	25.1
92	1440	72.5	95	1440	32.0	100	1440	42.2

Table 6.6 Swelling data for Marigold Tripletec Plus G44R Industrial Red Latex (H)

Marigold Tripletec Plus G44R Industrial Red Latex **(H)**								
NMP			GC 300			DSI 6000		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0
133	60	30.5	134	60	28.0	135	60	19.5
130	240	45.6	131	240	46.1	132	240	35.1
124	480	50.9	127	480	54.7	129	480	45.3
123	1440	43.2	126	1440	56.3	128	1440	41.4

Table 6.7 Swelling data for KCL 898 Butoject (J)

KCL 898 Butoject (J)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
127	73	0.2	132	73	1.1	137	73	3.1	146	60	0.2	142	110	11.4
126	221	0.5	131	221	1.6	136	221	3.8	145	280	0.1	141	280	19.7
125	328	0.4	130	328	2.0	135	328	5.2	144	480	0.2	140	480	28.0
124	480	0.6	129	480	2.4	134	480	6.7	143	1440	0.7	138	2880	34.9
123	1440	0.9	128	1440	3.3	133	1440	10.1						

Table 6.8 Swelling data for KCL 727 Nitopren (L)

KCL 727 Nitopren (L)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
222	60	27.8	226	60	12.8	230	60	9.4	234	60	12.5	242	110	46.2
223	280	71.8	227	280	26.1	231	280	19.3	235	280	26.1	241	280	69.4
224	480	107.7	228	480	34.2	232	480	18.2	236	480	44.8	240	480	123.9
225	4320	294.2	229	4320	97.9	233	4320	55.0	237	4320	175.6	238	2880	207.7

Table 6.9 Swelling data for KCL 717 Nitopren (M)

KCL 717 Nitopren (M)								
NMP			GC 300			DSI 6000		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0	0	0	0.0	0	0	0.0
111	71	52.4	116	71	12.3	121	71	11.8
110	137	80.0	115	137	19.4	120	137	19.3
109	230	147.5	114	230	24.9	119	230	26.2
108	480	211.0	113	480	42.3	118	480	32.5
107	1440	233.0	112	1440	83.5	117	1440	58.8

Table 6.10 Swelling data for Marigold Medical S340 (N)

Marigold Medical S340 (N)								
NMP			GC 300			DSI 6000		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0
159	60	5.6	160	60	23.7	161	60	26.9
156	240	6.0	157	240	27.8	158	240	28.5
151	480	8.2	153	480	32.0	155	480	47.3
150	1440	7.0	152	1440	30.7	154	1440	42.4

Table 6.11 Swelling data for Ansell Edmont 35-405 proFood (S)

Ansell Edmont 35-405 proFood (S)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
175	60	0.2	176	60	5.2	177	60	10.0	177	60	12.9	185	110	4.1
171	240	-0.2	172	240	1.4	174	240	1.3	178	280	6.0	183	280	0.0
167	480	0.0	165	480	2.6	170	480	4.3	179	480	0.0	182	480	0.0
164	1440	0.0	166	1440	4.4	169	1440	1.4	180	1440	1.3	181	2880	1.4

Table 6.12 Swelling data for North Silver Shield (T)

North Silver Shield (T)														
NMP			GC 300			DSI 6000			Graffiti Gone CR-GR1			Blitz GS		
Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change	Sample ref number	Time	% Mass Change
0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0	0	0	0.0
190	60	0.6	194	60	1.6	198	60	0.3	208	60	2.2	242	110	46.2
191	280	0.3	195	280	2.2	199	280	1.5	209	280	9.1	241	280	69.4
192	480	0.0	196	480	0.3	200	480	1.3	210	480	0.0	240	480	123.9
193	1440	0.9	197	1440	2.5	201	1440	10.9	211	1440	0.9	238	2880	207.7

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