REMOVAL OF CHEMICAL CONTAMINATION FROM VEHICLES BY EXPOSURE TO SUN AND WIND

DENYS AMOS*, RAY C. BOSTON[1], PETER J. GRAY and BRIAN LEAKE

DSTO, Materials Research Laboratory, P.O. Box 50, Ascot Vale, Victoria 3032 (Australia)
[1]*Computer Science Program, Murdoch University, Murdoch, W.A. 6150 (Australia)*

Summary

A computer model is presented which describes the desorption of a liquid chemical of intermediate volatility from vehicles in an enclosed chamber. The initial contamination level may be derived by measurement of the concentration of the desorbing-chemical vapour. The model has been applied to both alkyd and polyurethane painted vehicles and used to determine the residual contamination remaining on vehicles after exposure to sun and wind. An estimate of the weathering time necessary to reduce the hazard level to safe levels is made. The kinetics of evaporation of liquid simulant from painted surfaces and loss of simulant vapour from an enclosed chamber are also discussed.

1. Introduction

Chemical spillages are not uncommon in modern society where large volumes of industrial chemicals are transported by rail or by road. Considerable effort is expended in cleaning up spillages from accidents and on decontamination of the transport vehicles and surrounding terrain. Personnel carrying out decontamination frequently must wear protective clothing and respirators or self contained breathing apparatus as protection against toxic vapours. This protective equipment imposes a severe physiological burden on personnel due to heat stress and limits the effective operating time for an individual. The problem is exacerbated in warm climates and greatly reduces the time which can be spent in protective clothing while undertaking physical work. Any process which helps in the removal and reduction of contamination will reduce the requirement for decontamination and also will reduce the time during which personnel must wear protective clothing. Removal of contamination from surfaces through the natural processes of weathering by sun and wind will reduce the hazard from contaminated equipment.

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*Author to whom correspondence about this paper should be addressed.

During summer throughout Australia the input of solar radiation on to a surface can be as high as 900–1000W/m^2 giving rise to temperatures on metallic surfaces in the range 50–60°C. In combination with wind, such conditions accelerate the removal of chemical contamination from equipment through evaporation and may reduce or eliminate the need for decontamination. The present study investigates the removal of contamination from vehicles by exposure to sun and wind. To achieve this, a computer model has been developed to quantify simulant desorption from vehicles in an enclosed chamber. The model is used to determine the residual contamination remaining on vehicles after exposure to natural weathering for various times.

During the course of this study we also examined the kinetics of the evaporation of a chemical simulant, methyl salicylate (MS), from painted surfaces and from the chamber itself. The desorption of simulants from the painted surfaces of vehicles inside a sealed chamber constitutes a two stage process:

(1) The evaporation of simulant from the contaminated surface into the surrounding chamber.

(2) Diffusion by concentration imbalance out of the chamber.

Using measurements in a temperature-controlled chamber, we have been able to infer the nature of the evaporative processes for two different paint systems.

2. Experimental

2.1 Painted test plates

In the first series of studies two sets of painted steel panels were prepared with dimensions 75.0 mm $\times$ 75.0 mm $\times$ 1.25 mm according to specification [1]. The paints used were those commonly applied to Army vehicles, i.e. matt olive drab alkyd and aliphatic polyurethane. The painted panels were weathered outside for three months before use. Drops of MS ($30 \times 1\ \mu l$) were applied to the panels. These were then placed inside the chamber in two positions, horizontal and vertical, to simulate the orientation of the major surfaces of the vehicles. The rate of evaporation of MS from the panels was measured directly by weight loss. Four replicates were used for each orientation giving a total of eight measurements for each paint system.

2.2 Desorption chamber

The chamber in which the studies were carried out was constructed of stainless steel and was thermally insulated and temperature controlled. Total volume of the chamber was 93 m^3. Mechanical circulation of the air inside the chamber ensured rapid mixing of desorbing vapour.

Methyl salicylate (MS) was chosen as a simulant because of its intermediate volatility. The concentration of MS in the chamber decreased due to small leaks and to adsorption on the chamber walls. To determine the kinetics of the decay of simulant concentrations in the chamber, MS vapour (5 g) was re-

leased into the chamber by rapid vaporisation of liquid applied from a burette onto a hotplate.

2.3 Analysis

Methyl salicylate vapour concentrations were monitored by sampling into propylene glycol in sequential sampler bubblers. The sequential samplers each held 12 bubblers containing 5 ml propylene glycol as the absorbing medium and were programmed to sample the chamber over a 24 or 40 hour time span. The bubbler contents were analysed subsequently for MS by UV spectroscopy.

2.4 Vehicles

The vehicle chosen was the in-service Landrover complete with canvas canopy and rubber tyres. We investigated two paint systems; in-service Matt Olive Drab Alkyd paint or Low Gloss Olive Drab Aliphatic Polyurethane paint (PUP) to Australian Government Paint Committee Specification GPC-P 154/3. The paint formulations are detailed in Ref. (1).

Methyl salycilate containing Orasol Brilliant Fast Red (0.1%) and Tinopal SWN Conc (0.1%) as visual and fluorescent tracers respectively was sprayed onto the side, front and windscreen of the Landrover from a hand-held pressurised sprayer. The contamination density was determined by collection of sprayed MS on felt pads (100×100 mm); after contamination these were removed for analysis. The quantity of MS on the felt pads was determined by ethanol extraction and spectrophotofluorimetric analysis of the Tinopal SWN tracer in the extract.

The contaminated vehicle was driven into the sealed chamber which was temperature controlled at $20 \pm 1 °C$. Methyl salycilate desorbing from the vehicle was monitored by collection for later analysis in four sets of sequential samplers arranged around the vehicle.

In the studies on decontamination through weathering, the contaminated vehicles were exposed to sun and wind under Melbourne summer conditions in January, February and March for 30, 60 and 90 minutes to enhance removal of contamination. The mean insolation was 0.8 kW m^{-2}, mean wind speed 1.45 m s^{-1} and mean surface temperature 46°C.

Analysis of all data about the desorption of MS from vehicles in the chamber was carried out by using CONSAM which is the interactive version of the SAAM modelling program and allows the user to develop mathematical models to fit experimental data [2].

3. Results

3.1 Methyl salycilate evaporation from painted panels

Using measurements in the controlled chamber we have studied the nature of the evaporative processes for two paint systems. Examination of the evap-
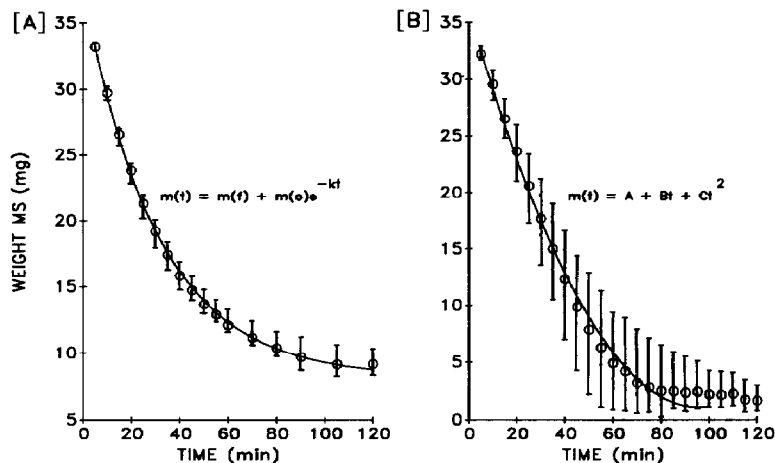
Fig. 1. Evaporation of methyl salicylate from [A] alkyd surfaces and [B] from polyurethane surfaces. Plates were oriented horizontally. Results are shown as the means and maximum and minimum of four replicates.

oration of simulant from horizontal painted plates is shown in Fig. 1, which shows the evaporation of methyl salicylate simulant from alkyd and polyurethane (PUP) painted surfaces; each plot is the mean of four replicates.

There are obvious differences in properties between the two paint surfaces. The evaporation of MS from the alkyd painted plates is very reproducible while the PUP plates show considerable variation. The systematic variation in the PUP experiments may represent "beading" of the simulant on the painted surface. The results for the vertical plates were similar.

3.2 Kinetics of MS loss from chamber

Figure 2 shows the rate of decay of the MS vapour in the chamber. A first order exponential equation is also plotted for comparison. This shows that the rate of loss of MS from the chamber is not precisely described by first order kinetics.

3.3 Desorption of MS from vehicle

Vehicles were sprayed with MS as described in Section 2 and the cumulative desorption of MS into the chamber measured. Three levels of simulant contamination density were studied for each of the two painted vehicles. The vehicles were not subject to weathering in this series and were placed in the chamber immediately after contamination was complete. The simulant desorption data for vehicles with varied contamination densities are given in Fig. 3A for alkyd painted vehicles and in Fig. 3B for polyurethane painted vehicles. The data were used to develop the model and to relate initial contamination
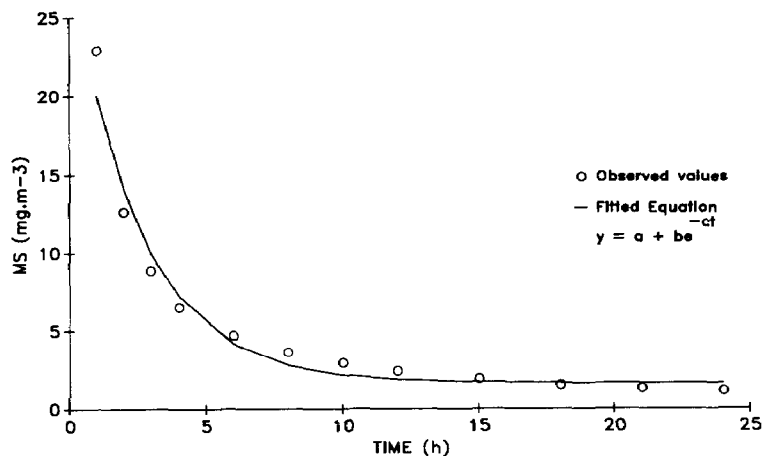
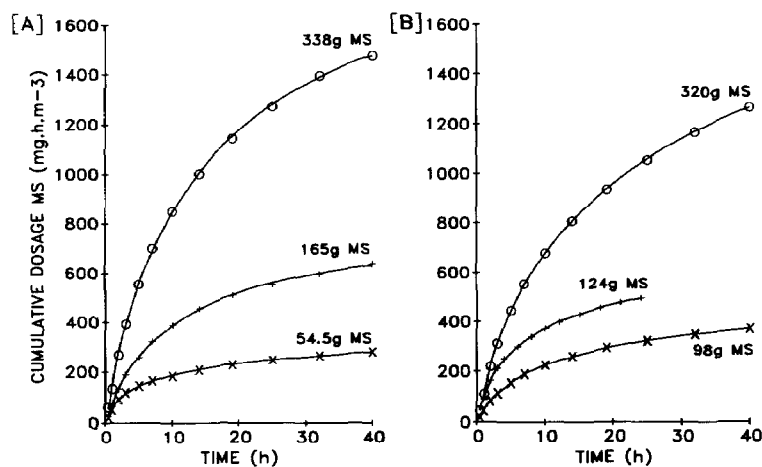Fig. 2. Loss of methyl salicylate from chamber.

Fig. 3. Desorption of MS from [A] alkyd vehicles and [B] from polyurethane vehicles in chamber — experimental data and CONSAM fitted equations. The unbroken line is the CONSAM fit.

levels to parameters derived from the model. The fitted plots were produced from the experimental data using CONSAM and the developed empirical model (eqn. (1) in Section 4.2).

3.4 Desorption of MS from contaminated vehicles after weathering

Total cumulative dosages of MS from vehicles after exposure to sun and wind are given in Fig. 4 which illustrates the rate at which MS desorbed from alkyd and polyurethane coated vehicles respectively after weathering for 30,

60 and 90 minutes. The fitted plots were produced from a developed empirical model by using CONSAM as in Section 3.3 above.

4. Modeling studies

4.1 Modeling of evaporation of MS from plates

The evaporation of methyl salicylate from alkyd painted plates followed first order kinetics and hence the equation

$$m_t = m_f + m_0\, e^{-kt}$$

best fitted the data, where m_t is the mass of simulant remaining at time t and k is the first order evaporation rate constant. The initial dose applied to the plates is $(m_0 + m_f)$. The fitted parameters and associated standard errors are shown in Table 1.

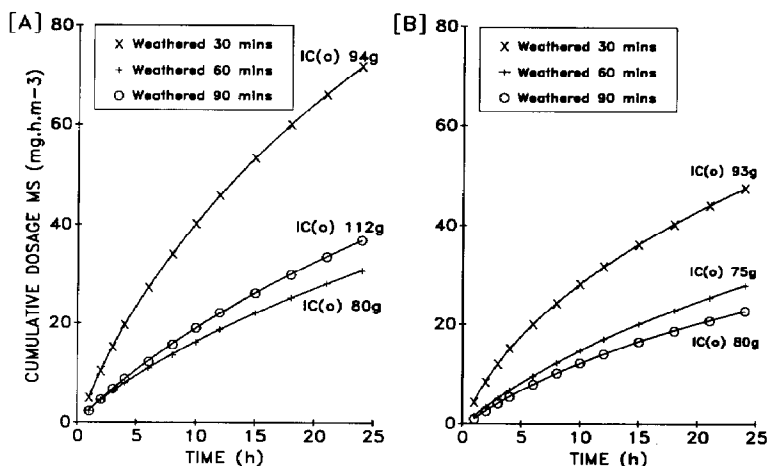The parameter m_f represents the amount of MS remaining on the plates as

Fig. 4. Cumulative dosage of MS from [A] alkyd vehicles and [B] from polyurethane vehicles after weathering — experimental data and CONSAM fit. The unbroken line is the CONSAM fit.

TABLE 1

Kinetic parameters for the evaporation of MS from vertical and horizontal alkyd painted plates

Plate orientation	Parameter			
	m_f (mg)	m_0 (mg)	k (min^{-1})	$m_f/(m_f+m_0)$
Vertical	8.15 ± 0.20	29.62 ± 0.18	0.033 ± 0.0006	0.21 ± 0.005
Horizontal	7.89 ± 0.18	30.11 ± 0.69	0.040 ± 0.0014	0.22 ± 0.004
Mean	8.02 ± 0.19	28.86 ± 0.43	0.036 ± 0.0010	0.21 ± 0.007

$t \to \infty$. This suggests that approximately 20% of the MS is absorbed very strongly by the painted surface. The value of k is highly reproducible.

However, the evaporation of MS from PUP plates could not be described adequately by the first order model. The quadratic equation

$$m_t = A + Bt + Ct^2$$

best fitted the data where m_t is the mass of simulant remaining at time t. Thus

$$m_0 = A$$

and

$$\frac{dm_t}{dt} = B + 2Ct$$

which, provided t is small, $|B| \gg C$ and $B < 0$, reflects predominantly a zero order kinetic evaporative loss profile for polyurethane paint. The fitted parameters and associated standard errors are detailed in Table 2. The value of A is the initial level of simulant.

The model proposed for evaporation can therefore be visualised as follows:
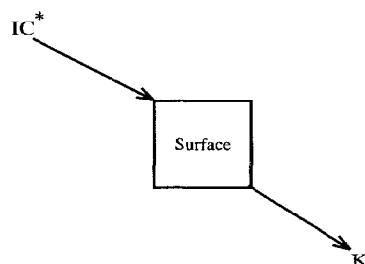
where IC^* denotes the initial contamination level and K the rate constant for loss by evaporation. This model only has a limited range of accuracy and will not apply for very small or very large values of surface contamination.

By making two assumptions, that is

TABLE 2

Kinetic parameters for the evaporation of MS from vertical and horizontal PUP painted plates

Plate orientation	Parameter		
	A (mg)	B (mg min^{-1})	C (mg min^{-2})
Vertical	35.76 ± 0.54	-0.79 ± 0.041	0.0036 ± 0.00067
Horizontal	36.17 ± 0.59	-0.74 ± 0.022	0.0039 ± 0.00017
Mean	35.96 ± 0.56	-0.76 ± 0.032	0.0038 ± 0.00042

(1) The loss profiles of alkyd and polyurethane are similar;
(2) Linking processes 1 and 2 directly is reasonable (implying instantaneous mixing of desorbed simulant)

it would appear that a complete specification of simulant desorption kinetics can be described. As a result, values of *IC* (the initial contamination level) can be derived from the experimental data.

The model of the complete system incorporating evaporation from the contaminated surface and loss from the chamber is therefore:
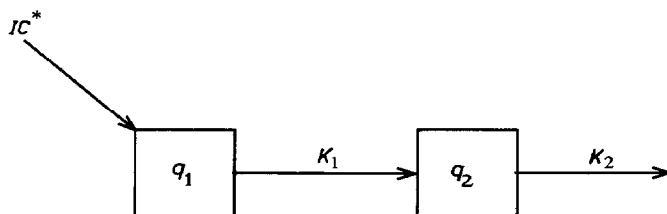
where IC^* denotes initial condition, q_1 surface level of simulant, K_1 evaporative profile of simulant (linear on alkyd, zero order on polyurethane), q_2 simulant level of chamber, and K_2 loss profile of simulant from chamber.

4.2 Modeling of simulant desorption from unweathered vehicles in chamber

As mentioned above, the loss of simulant from the chamber does not follow first order kinetics but rather some complicated kinetic profile. Evaporation of MS from the painted surface of the vehicle is first order for alkyd vehicles and zero order for polyurethane painted vehicles. Polyurethane painted vehicles have considerable surface areas of different materials which may desorb with first order kinetics and tend to mask the behaviour of the polyurethane paint. Furthermore the constitution and gloss level of the painted surface has a considerable influence on the desorption and evaporation kinetics.

The model finally accepted was

$$Ct = P_1[1 - \exp(-P_2(t-P_4)^{P_3})] \tag{1}$$

where P_1 is a measure of the coating level of the simulant, P_2 is a first-order parameter (provided $P_3 \approx 1$), P_3 is a measure of deviation from linear kinetics, and P_4 is an offset allowing for errors associated with recording early observations for the experiment.

Figure 3 summarises the fits of the above model to a series of studies relating to 3 levels of simulant contamination density for each of the two painted vehicle surfaces. The vehicles were not subject to weathering in this series and were placed in the chamber immediately contamination was complete.

With the initial conditions (initial simulant contamination level) known for each experiment, the estimated P_1 for studies in which neither P_2 nor P_3 was constrained was regressed on simulant dosage. To the initial contamination level P_1 is related as follows:

TABLE 3

Derived values of P_1, contamination level ($IC_{(w)}$) and decontamination efficiencies (DC) after weathering for alkyd and polyurethane painted vehicles

Paint type	Weathering time (min)	P_1	$IC_{(0)}$[a] (g)	$IC_{(w)}$ (g)	DC (%)
Alkyd	30	148.2	94	26 (1.1)[b]	72
Alkyd	60	103.6	80	17 (4.9)	79
Alkyd	90	92.3	112	15 (2.3)	87
PUP	30	116.8	93	20 (1.9)	79
PUP	60	60.3	75	8 (1.3)	89
PUP	90	42.8	94	5 (0.8)	95

[a]$IC_{(0)}$ is the mass of MS applied to the vehicle by spraying.
[b]Standard error.

$$P_1 = 4.91 \ (IC) + 20.2 \tag{2}$$

where IC is the initial contamination level.

4.3 Modeling of simulant desorption after weathering

The data were fitted by using CONSAM to the developed empirical model (eqn. 1) to give the values of P_1 shown in Table 3. Values of $IC_{(w)}$, the contamination level after weathering were calculated from eqn. (2).

In Table 3 we also present the decontamination efficiency of exposure to sun and wind in the summer months at latitude 38°S; the initial contamination densities were in the range 6–9 g m^{-2}. It is evident that weathering for periods exceeding 90 minutes is an effective way to reduce contamination even in temperate latitudes.

5. Discussion

The initial work showed that the evaporation of MS from alkyd painted plates followed first order kinetics which were consistent under replication. The data for the evaporation of MS from polyurethane paint showed a zero order kinetic loss profile. That simple first order kinetics do not describe the evaporation of simulants from both alkyd and polyurethane vehicles is evident from considerations of the nature of change of the surface areas of the simulant as it evaporates. In our estimation it is likely that the nature of simulant kinetics will be initially zero order, then, as the simulant evaporates to a stage where its surface area is reducing linearly, first order, and finally, where heterogeneous holes of completely evaporated simulant start to appear, non-linear kinetics.

The variations in the fitted parameters detailed in Table 2 are consistent

with the observed behaviour of liquids on polyurethane surfaces. Local anomalies in the surface properties of the low gloss paint lead to variations in the rate of spreading of the applied liquids. In particular, on some areas of the PUP panels the applied simulant remained as discrete drops, whereas in other areas the simulant spread over the surface.

Other materials present on vehicles, such as canvas and rubber, may complicate the kinetics of simulant desorption. Vehicles are not naturally composed of entirely planar surfaces and chemical contamination can remain held by capillary action in cracks and crevices even when the major part of the vehicle surface is contamination free. However, such cracks and crevices form a minor part of the total vehicle surface and outward diffusion of contamination vapour is accelerated by the increased temperatures resulting from solar radiation.

There is no way of discerning cutoffs between these phases of evaporation and such an approach would not be of lasting utility. Even if the exact kinetics were isolated, it may be of more use to explore an empirical approach, since a loss profile may span several regions of applicability of a mechanism. Furthermore we are more concerned with accuracy of prediction than with desorption mechanisms. We therefore attempted some empirical experimentation with models potentially flexible enough to absorb the key kinetic features alluded to above and to explain all the data for both painted surfaces.

From the modeling study we may infer the following:

(1) The model defined in eqn. (1) describes well simulant desorption from the vehicles for both types of surfaces for the duration of the experiment.

(2) The unconstrained fits were substantially superior to the constrained fits.

(3) Desorption of simulant from polyurethane was better described by using the model than from alkyd.

(4) Early parts of the response, perhaps associated with zero order kinetics were less well described than later parts of the response for both painted surfaces.

(5) In regions where accurate estimates of the response were needed, the model fitted extremely well.

(6) For both surfaces the value of P_2 was about 0.2 which was within the range of the first order kinetics reflected in Table 1 (0.037 ± 0.001) and the zero order kinetics reflected in Table 2 (0.76 ± 0.03). This suggests a first-order kinetic approximation with a rate parameter close to this value.

(7) The value for P_3 was around 0.7 for both surfaces suggesting that in most cases deviation from linear kinetics may be small.

(8) For unconstrained fits the relative error in the fit of the last two points was less than 0.5%.

(9) As postulated P_1 bore a close relationship to the initial contamination level and in fact P_1 was well described for both painted surfaces by eqn. (2). This relationship was inferred from the data obtained on both types of

paint surfaces. As a result, for vehicles where the initial contamination level is unknown, it may be derived from calculation of P_1.

It is clear that weathering is much more effective in removing contamination from polyurethane than from alkyd painted vehicles. This is despite the large area of canvas canopy on the test vehicles. Vehicles in which the exterior is mainly painted metal may weather more rapidly. Commercial transport vehicles are coated with a variety of paint types ranging from twin-pack glossy polyurethane to acrylic. The properties of such paints, as far as absorption of chemical contamination is concerned, ranges from chemical resistant to chemical absorptive. The PUP and alkyd paints detailed in our study were chosen to cover the extremes of paint types and because their formulations are well documented. Commercial paint systems are expected to fall between these two types but their formulations remain commercially confidential.

Extrapolation of the data detailed in Fig. 5 shows that a level of 3% residual contamination would be achieved by 2 hours weathering for polyurethane and 4 hours for alkyd vehicles. For all but the most toxic of chemicals this would be sufficient to reduce the hazard to below the minimum risk value. For a chemical with an ICt_5 of 50 mg m^{-3} min such a period of weathering would give a 24 hour safe exposure period.

The corollary is that the minimum risk values for most chemicals may be achieved by weathering under climates similar to that of South Eastern Australia in the summer. Alkyd painted equipment would require exposure for 4 hours and PUP painted equipment for 2 hours to achieve safe levels. In the tropics the weathering process would be accelerated and be more efficient due to the higher temperatures and solar radiation. In the cooler or more temperate climates experienced in Europe and North American during the cooler seasons
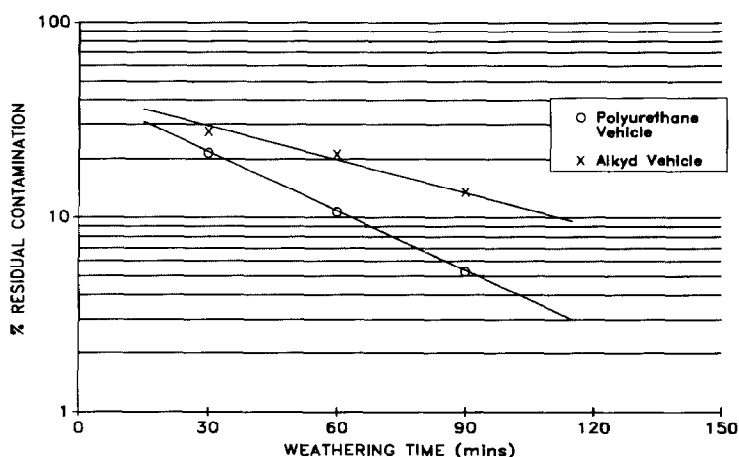

Fig. 5. Plot of percentage residual contamination vs. weathering time.

the weathering times necessary to achieve minimum risk exposure values would be more prolonged. In such instances removal of contamination by applied chemical or physical decontamination processes would be advantageous.

References

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