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The supply and use of CI Solvent Red 164 as a penetrant dye in the detection of cracks in metal components

Final update for 21st WATCH Meeting, 25th October 2011

Previous Paper: WATCH/2008/1: The supply and use of CI Solvent Red 164 as a penetrant dye in the detection of cracks in metal components

Issue

WATCH/2008/1 reviewed the use of CI Solvent Red 164 as a penetrant dye in the detection of cracks in metal components and reached the following conclusions:

- The paucity of hazard and exposure data on CI Solvent Red 164 was disappointing;
- Based on the limited hazard data available, it was appropriate to consider that this substance might have carcinogenic potential: it should therefore be subject to the same exposure control approach as for other suspect carcinogens;
- Exposure data were currently lacking to inform on the degree to which current practices and associated exposures conform to these expectations;
- Issues required more attention from industry;
- Recommendation for a potential substitute could not be made as there was insufficient hazard and exposure information available for the potential alternatives.

Background

This paper is provided to inform WATCH members on actions taken by HSE and industry stakeholder partners to address the above issues. The information provided is drawn from the three short update papers (dated the 24th October 2008, 24th February 2009 and 12th June 2009) previously presented to WATCH, plus additional data generated since.

Questions have been raised over the use of CI Solvent Red 164 due to the potential for this dye to metabolise within the body and liberate its aromatic amine precursors including ortho-toluidine (a Category 2 carcinogen linked with an increased incidence of bladder cancer) and aniline (a Category 3 carcinogen). The carcinogenic potential of ortho-toluidine was summarised in Annex 2 of WATCH/2008/1).

Hazard and exposure data

HSE have previously presented hazard and exposure data to WATCH on 24th October 2008, 24th February 2009 and 12th June 2009. Prior to issue of this update paper, HSE are not aware of the production of any new hazard or exposure data on CI Solvent Red 164 by industry.
A poster paper was brought to HSE's attention (received from Sheffield Occupational Advisory Service in 2010) that summarised a study on nine German metal crack testers using azo dye-based sprays who had suspected occupational bladder cancer [1]. Results showed that the period between first exposure and diagnosis (the latency period) was between 17 and 45 years. Initial exposures were from 1957 – 1986. The conclusion of this work was that *'every bladder cancer patient with a history of metal-related jobs should be explicitly asked for crack testing'.*

HSE is aware that researchers at the University of Sheffield are to conduct a 3-year investigation (funded by Yorkshire Cancer Research) into potential links between bladder cancer in workers using dyes in crack testing of metals in the region's metal industries (http://www.yorkshirecancerresearch.org.uk/news/news_item.aspx?id=209).

In 2008 WATCH agreed that HSE had insufficient exposure data available for users and suppliers of dye penetrants containing CI Solvent Red 164. A programme of work was initiated to build up a profile of exposure data for these two potentially exposed groups. This programme of work included quantitative measurements of worker exposure to the potentially carcinogenic aromatic amine metabolites - aniline and ortho-toluidine, using biological monitoring (BM). Workers in all exposed or potentially exposed areas agreed to give pre-, and post-shift urine samples for at least one day of work activity.

In 2007 and 2008, HSE visited all five formulators of azo dye containing liquid penetrants identified in WATCH/2008/1. One formulator has however, ceased to trade. The four remaining formulators continue to market their azo dye containing liquid penetrants and all confirm pre-registration with REACH.

On completion of the survey of formulators, HSE then visited manufacturing sector sites engaged in non-destructive testing (NDT). Two different types of worker carrying out NDT were targeted; these were foundry workers inspecting castings for defects and independent consultant examiners. Three foundries agreed to participate in this study. Following on from the last WATCH update (12th June 2009), the partnership with the British Institute of Non-Destructive Testing (BINDT) indicated that up to 50 independent consultant examiners would potentially participate, however, urine samples were received from only three.

The BM results for all workers sampled are presented in Appendix 1 (Tables 1 to 3).

Guidance to industry

In 2008, HSE Metals and Minerals sector published a Sector Information Minute SIM 03/2008/10, '*The use of liquid dye penetrants containing the azo compound CI Solvent Red 164 in the detection of flaws or cracks in metal components.'* This document provides guidance for industry users and HSE and Local Authority inspectors on the precautions to be taken when using a liquid dye penetrant containing the azo compound CI Solvent Red 164, and remains current.

HSE made contact with the Foundry, Engineering and NDT user industry groups to make them aware of SIM 03/2008/10.

Under the Foundry industry's Safety and Health Foundry Targets Initiative (SHIFT) a safety alert was produced advising member companies of the issues covered by the WATCH 2008 review and the publication of SIM 03/2008/10.

Potential substitutes

The last WATCH update (12th June 2009) reported that one formulator was actively pursuing a substitute dye. However this dye has a high sulphur content that can cause additional defects in stainless steel. This formulator also stated that they had exhausted all the possible red dye alternatives, and they were encouraging NDT examiners to use fluorescent dyes wherever possible.

The same formulator has since introduced a non-azo blue dye penetrant. The dye (reported to be based on a soya oil) is present at a concentration of 18.4% in an ester formulation. The company have classified this formulation (in aerosol form) as R36 – irritating to eyes. They report that they are struggling to sell this dye due to its higher cost. Photographs of 2 different work pieces, one tested with the red dye and the other with the blue dye for the presence of defects are provided in Appendix 2. The photographs are provided for information purposes only to demonstrate how defects are revealed by use of the dyes in question.

HSE are not aware of any further initiatives to develop a dye substitute.

Discussion of results

The data set presented at Appendix 1 indicates that urinary levels of ortho-toluidine and aniline for the workers employed in the *formulation* of liquid penetrants containing the azo dye, CI Solvent Red 164 were no higher than urinary levels of these two substances found in the general population. The elimination half-life of aniline and ortho-toluidine in urine is around 3 hours. Assuming the release of aniline or ortho-toluidine from the azo dye does not increase the half lives significantly any aniline or ortho-toluidine found in pre-shift urine samples would be expected to reflect background levels rather than

previous day occupational exposure. The usual time for collecting urine samples for substances with a half life of 3 hours is at the end of exposure. If the release of the amines from the azo dye significantly increased the apparent half life then we might expect higher levels in pre-shift samples than post-shift samples.

The only notable exception was worker C7 (where significantly higher levels of aniline were measured – however these results may have been subject to error as the sample was significantly diluted prior to analysis).

For workers involved in *NDT* work (both foundries and independent testers) urinary levels of both measured substances were no higher than those in the general population apart from elevated aniline levels measured in workers E2, F3, G1 and I2. However the urine sample from worker G1 contained low creatinine levels and hence should be treated with some caution. The concentration of analytes in urine can vary depending on the state of hydration of the worker. To try and compensate for this it is common practice to adjust an analyte concentration by dividing its concentration by the concentration of creatinine. This assumes the analyte is excreted in the same way as creatinine and for aniline and ortho-toluidine this is not certain. However, creatinine adjustment is unlikely to introduce significant errors except at the extremes of the concentration range so adjustments with 'low' (<3 µmol/l) and 'high' (>30 µmol/l) creatinine concentrations are flagged as 'low' or 'high'. In such cases the result should be interpreted with caution (ie.unless results are supported by other data and do not take any action other than requesting a repeat sample).

Conclusion

Of the 127 BM results obtained for aniline, six were above the background range and of these three can be discarded due to uncertainties caused by dilution and low creatinine. This leaves three values (E2 pre, F3 post and I2 pre), and among 127 results this might be expected on a statistical basis. If these three results are indicating exposure then it is much less (<5%) of the guidance value.

None of the BM results for ortho-toluidine were higher than those in the general population with the majority being at the non-detected level.

Overall, the findings from the limited data set provided in this study do not appear to present a cause for concern regarding the potential levels of exposure to CI Solvent Red 164 during its formulation and use in accordance with the precautionary measures listed in SIM 03/2008/10.

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July 2011

References

[1] Bladder cancer in crack testers applying azo dye-based sprays to metal bodies (Selinski S., *et al*. (received from Sheffield Occupational Advisory Service in 2010)

APPENDIX 1

Biological monitoring (BM) results from quantitative assessment of worker exposures at the formulation of liquid dye penetrants containing the azo compound CI Solvent Red 164
to the potential carcinogenic metabolites aniline and ortho-toluidine.

Table 1 - Biological monitoring results for the formulators of liquid dye penetrants

Formulator	Worker	Work details	Sample details	Aniline (µmol/mol creatinine)	o-Toluidine (µmol/mol creatinine)
A	A1	Mixing penetrant solution and filling containers for one hour	pre-shift day 1	8	2
			post-shift day 1	8	2
			pre-shift day 2	9	2
			post-shift day 2	7	2
	A2	Mixing penetrant solution and filling containers for one hour	pre-shift day 1	4	1
			post-shift day 1	3	1
			pre-shift day 3	3	1
			post-shift day 3	4	1
	A3	Mixing penetrant solution and filling containers for one hour	pre-shift day 2	6	2
			post-shift day 2	9	2
			pre-shift day 3	7	1
			post-shift day 3	8	2
B	B1	Transferring concentrate for 20 mins	pre-shift day 1	no analysis	ND
			post-shift day 1		
	B2	Mixing penetrant solution and filling containers for 1 hr 30 mins	pre-shift days 1,2,3,5		
			post-shift days 1,2,3,5		
	B3	Mixing penetrant solution and filling containers for one to two hours	pre-shift days 5,6,7,8,9		
			post-shift days 5,6,7,8,9		
C	C1	Transferring penetrant solution and filling containers for three hours	pre-shift day 2	2	0.4
			post-shift day 2	3	0.5
			pre-shift day 3	3	ND
			post-shift day 3	4	ND
	C2	Transferring penetrant solution and filling containers for three hours	pre-shift day 1	6	ND
			post-shift day 1	2	ND
			pre-shift day 3	2	ND
			post-shift day 3	2	ND
	C3	Transferring penetrant solution and filling containers for three hours	pre-shift day 1	3	ND
			post-shift day 1	8	ND
	C4	Transferring penetrant solution and filling containers for three hours	pre-shift day 1	4	ND
			post-shift day 1	4	ND
			pre-shift day 3	3	ND
			post-shift day 3	10	ND
	C5	Transferring penetrant solution and filling containers for three hours	pre-shift day 1	ND	ND
			post-shift day 1	2	ND
	C6	Transferring penetrant solution and filling containers for three hours	pre-shift day 1	6	ND
			post-shift day 1	2	ND
			pre-shift day 3	7	ND
			post-shift day 3	6	ND
	C7	Transferring penetrant solution and filling containers for three hours	pre-shift day 3	41 +	ND
			post-shift day 3	61 +	ND
	C8	Transferring penetrant solution and filling containers for three hours	pre-shift day 3	1	ND
			post-shift day 3	2	ND
D	D1	Transferring concentrate for one hour	pre-shift day 1	2	ND
			post-shift day 1	3	ND
	D2	Transferring concentrate for one hour	pre-shift day 2	4	ND
			post-shift day 2	6	ND
HSE Reference range (unexposed population)				< 10	< 5
Guidance Value				~900 (German BAT)	N/A

Note:

(1) Sampling days are not consecutive calendar days
(2) The detection limit of the assay used at Formulator B was approximately a factor of 2 higher - and was roughly equivalent to 10 µmol/mol - so still capable of detecting any levels above background.

(3) Samples marked + should be interpreted with care as, due to very low sample volume, results are from significant dilution. Repeat sampling is recommended and will be undertaken. Aniline results are still very low compared with the German Guidance Value 900 (approx) µmol/mol creatinine.

Formulator A process description

The concentrate dye is manually dispensed from a 100 litre drum into a 25 litre container which is then carried to the mixing vessel. The concentrate is then poured into a mixing vessel. A lid is then secured onto the mixing vessel whilst mixing takes place. The formulated product is then transferred by gravity feed from the mixing vessel to either a semi-enclosed aerosol filling station (provided with LEV) or directly into 5 or 25 litre tins in the open workroom. Workers wear neoprene chemical protective gloves and negative pressure half-mask RPE fitted with AP12 filters.

Formulator B process description

The concentrate dye is delivered from a 1 tonne IBC to the mixing vessel via a vacuum transfer system comprising a lance inserted into the IBC (LEV is provided at this point) and a sealed transfer line running to the mixing vessel. Mixing is carried out remotely and the formulated product dispensed via gravity feed to 1 tonne IBCs or 200 litre drums. LEV is provided at the fill point and the process is housed in a large naturally ventilated hall. Workers wear natural rubber chemical protective gloves, nitrile gauntlets, chemical resistant clothing and negative pressure half-mask RPE.

Formulator C process description

This workplace does not handle the red dye concentrate. Pre-formulated red dye solution is delivered in either 1 tonne IBCs from Formulator D or 100 litre drums (imported and delivered unopened) to be made up into 440 ml aerosol spray cans. The red dye solution is transferred to the aerosol spray can filling station supply tank via a vacuum transfer system comprising a lance inserted into the IBC or drum (LEV is provided at this point) and a sealed transfer line running to the supply tank. Aerosol cans, delivered automatically to the filling point by conveyor are filled and sealed remotely in a fully enclosed aerosol filling station provided with LEV. Workers wear poly cotton overalls and PVC or nitrile gloves.

Formulator D process description

The concentrate dye is imported and delivered unopened in 100 litre drums. It is subsequently transferred to an intermediate mixing drum and then on to a mixing vessel via a vacuum transfer system. This comprises a lance inserted into each drum (LEV is provided at each transfer) and then a sealed transfer line running to the mixing vessel. Mixing is carried out remotely and the formulated product dispensed via a pumped feed to 1

tonne IBCs for onward shipment to Formulator C. Workers wear poly cotton overalls and natural rubber chemical protective gloves.

Table 2 – Biological monitoring results for the foundry NDT workers

Foundry	Worker	Work details	Sample details	Result (µmol/mol creatinine)	
				Aniline	o-Toluidine
E	E1	NDT on castings (~6hrs exposure)	Pre-shift	2	ND
			Post-shift	9	ND
		NDT on castings (~2hrs exposure)	Pre-shift	1	ND
			Post-shift	2	ND
		NDT on castings (~8hrs exposure)	Pre-shift	1	ND
			Post-shift	1	ND
		NDT on castings (~8.5hrs exposure)	Pre-shift	1	ND
			Post-shift	1	ND
		NDT on castings (~6.5hrs exposure)	Pre-shift	2	ND
			Post-shift	2	ND
	E2	None given, presumed to be NDT testing (~4hrs exposure)	Pre-shift	8	ND
			Post-shift	1	ND
		None given, presumed to be NDT testing (~7hrs exposure)	Pre-shift	1	ND
			Post-shift	1	ND
		None given, presumed to be NDT testing (~7hrs exposure)	Pre-shift	1	ND
			Post-shift	1	ND
		None given, presumed to be NDT testing (~7hrs exposure)	Pre-shift	1	ND
			Post-shift	1	ND
		None given, presumed to be NDT testing (~2hrs exposure)	Pre-shift	14	ND
			Post-shift	1	ND
F	F1	Testing of castings (~1hrs exposure)	Pre-shift	1	ND
			Post-shift	2	ND
	F2	Dye pen testing (~2hrs exposure)	Pre-shift	7	ND
			Post-shift	5	ND
	F3	Dye pen testing (~1hr exposure)	Pre-shift	4	ND
			Post-shift	37	ND
G	G1	Dye pen chain links (8hrs exposure)	Pre-shift	No sample	No sample
			Post-shift	18 *	ND *
			Pre-shift	1	ND
			Post-shift	2	ND
	G2	Crack detection weld repair	Pre-shift	1	ND
			Post-shift	9	ND
		Crack detection weld repair (4hrs exposure)	Pre-shift	2	ND
			Post-shift	5	ND
		Crack detection weld repair (8hrs exposure)	Pre-shift	1	ND
			Post-shift	3	ND
		Crack detection weld repair (8hrs exposure)	Pre-shift	1	ND
			Post-shift	5*	ND*
		Crack detection weld repair (10hrs exposure)	Pre-shift	2	ND
			Post-shift	4	ND
	G3	Dye pen chain links	Pre-shift	No sample	No sample
			Post-shift	1#	ND#
		None given, assumed to be dye pen work	Pre-shift	1	0.8
			Post-shift	1#	0.4#
	G4	Welding and repairing castings	Pre-shift	No sample	No sample
			Post-shift	2	0.5
		Weld repair – Crack detection	Pre-shift	1	ND
			Post-shift	1	ND
		Weld repair – Crack detection (9hrs 20 min exposure)	Pre-shift	2	ND
			Post-shift	3	ND
HSE Reference range (unexposed population)				<10	<5
Guidance Value				~900 (German BAT)	N/A

* Low creatinine in sample
# High creatinine in sample

Foundry E process description – The casting to be tested is placed in a metal trough. Dye penetrant is applied by hand using a paintbrush and left to develop for ~ 30 minutes. The casting is then hosed down with water, the diluted penetrant draining into a bucket through a hole at the bottom of the trough. A developer is applied and left for a further 30 minutes before any cracks are examined. There is no LEV/forced general ventilation within the NDT area. PPE worn consists of proban overalls, safety glasses, safety boots and disposable nitrile gloves (changed at every stage of the process).

Foundry F process description – The casting is placed over a grid that is positioned above a drain leading to the main sewer. Dye penetrant (Jap water washable or Ardrox 907) is applied to the casting by either low pressure hand pump spray device or brush. This is rinsed off with water and compressed air is used to dry the cast. An aqueous developer is then applied by aerosol and left for 5 –30 minutes before the casting is checked. There is no LEV at the main NDT work area. A nearby bay (where NDT is occasionally carried out) has forced general ventilation. PPE worn consists of proban overalls, safety footwear and either general purpose or nitrile gloves.

Foundry G process description – NDT work is carried out on manganese castings and in the welding bays. Manganese castings are placed within an area cordoned off from a larger work area. The casts are arranged on a rack above a drainage tray, the dye penetrant is applied using a brush and left to dry for ~ 15 minutes. They are then hosed down with water, the diluted penetrant entering a drainage tray where it runs into a crate. Developer is then sprayed over the casts. There is an extract fan in this area.

In the welding bay the dye penetrant is applied to defects from an aerosol can and left for 2/3 minutes before it is wiped off with a cloth. Developer is sprayed on and the cast inspected. LEV was present.

PPE worn in both areas consists of proban overalls, safety footwear, safety glasses, hearing protection and gloves. Gloves worn for manganese NDT have a nitrile coating on the exterior surface with welding gloves worn in the welding area.

Table 3 – Biological monitoring results for Independent testing companies carrying out NDT work

Company	Worker	Work details	Sample details	Result µmol/mol creatinine	
				Aniline	o-Toluidine
H	H1	100% DPI of 50 stems red solvent (2hrs exposure)	Pre-shift	3.3	ND
			Post-shift	1.9	ND
		100% DPI of lock screws (2hrs exposure)	Pre-shift	3.3	ND
			Post-shift	2.9	ND
	H2	8 off combuster chambers (0.5hrs exposure)	Pre-shift	2.9	ND
			Post-shift	ND	ND
		No details given	Pre-shift	ND	ND
			Post-shift	ND	ND
			Pre-shift	ND	ND
			Post-shift	ND	ND
I	I1	DPI training (4hrs exposure)	Pre-shift	5.1	ND
		No details given	Pre-shift	6.2	ND
	I2	No details given	Pre-shift	5.1	ND
		No details given	Post-shift	6.9	ND
		DPI training course (4hrs exposure)	Pre-shift	37.9	ND
			Post-shift	ND	ND
J	J1	Crack detection (1hr exposure)	Pre-shift	3.5	ND
			Post-shift	2.2	ND
	J2	Dye penetrant crack detection (2hrs exposure)	Pre-shift	6.4	ND
			Post-shift	5.3	ND
HSE Reference range (unexposed population)				<10	<5
Guidance Value				~900 (German BAT)	N/A

No contextual data provided

APPENDIX 2

Photographs of two different work pieces, one tested with the red dye and the other with the blue dye for the presence of defects.