One of the aims of REACh (Registration, Evaluation, Authorisation restriction of Chemicals) is to improve the flow of Health, Safety and Environmental communications from the manufacturers of chemicals to the end users. The product safety data sheet (SDS) is a tool for achieving this. One aspect for consideration when producing an SDS is the skin and eye irritating properties of the product.

The information on the SDS for the skin/eye irritating properties of mixtures such as metalworking fluids are determined according to the EU’s calculation procedure. However, synergetic or antagonistic effects between the product’s ingredients are difficult to calculate. Animal tests are also used, but are less acceptable due to unnecessary animal suffering. Several new non-animal tests are now being officially accepted and consequently Cimcool has undertaken large scale skin and eye irritation tests using these. This fulfils the company’s obligations to REACh, as well as the future GHS (global harmonised system) requirements.

The tests were performed on the products as supplied, in concentrated form. Metalworking fluids are typically diluted with water to concentrations between 5 and 10%. Skin contact occurs far more frequently with diluted products than with the concentrated form. Due to the frequent skin contact, skin irritation is a regularly occurring issue within the metalworking industry. Skin irritation prevention has always been an important objective for Cimcool and substantial tests have been conducted to exclude Cimcool metalworking fluids as a contributing irritant.

Cimcool’s first tests started back in the 1960s. Over the years new skin irritation tests have become available, including TEWL (Transdermal Water Loss) on human volunteers and BUS (Bovine Udder Skin) using cow’s udders. These tests are usually performed using diluted products. With many years’ of tribological experience, using tests that are state-of-the-art, Cimcool has developed metalworking fluids that are heading toward being completely skin compatible, thereby removing irritation issues.

Skin and Eye irritation according to European Union directive 1999/45/EC

Most water-miscible metalworking fluids are complex mixtures in order to give the product the required technical performance. A typical metalworking fluid may contain: Corrosion inhibitors such as alkanolamine borates, short chain carboxylic acid salts of alkanolamines, amides. Emulsifiers - such as fatty acid soaps of alkanolamines. Lubricants including mineral oil esters. And, biocides to retard fungal growth.

The principle for establishing skin/eye irritation according to the EU DPD is straight forward, at first sight. It is based on the raw material information and the concentration.

If you consider two ingredients of a metalworking fluid: monoethanolamine (8%) and biocide (3%). Both can be considered as corrosive to the skin/eye (R34). Using the EU’s calculation method this metalworking fluid would be classified as corrosive since the combined concentration is above 10%, the point above which the DPD states the product is corrosive. This calculation method, however, does not take neutralisation into account. The corrosive effects of the alkaline monoethanolamine are decreased with acidic materials such as boric acid and fatty acids.

In order to investigate the skin/eye irritation properties of metalworking fluid concentrates Cimcool performed independent irritation tests.
Eye irritation tests: CEET (Chicken Enucleated Eye Test)

Samples were examined for acute eye irritating/corrosive properties in an ex vivo screen using the chicken enucleated eye test. The purpose of this ex vivo study was to provide data on the irritancy of the substance after a single application to isolated eyes of slaughtered chickens. In this ex vivo bioassay, three parameters were measured to disclose possible adverse eye effects, namely corneal thickness (expressed as corneal swelling), corneal opacity, and fluorescein retention of damaged epithelial cells of the cornea. The measurement of corneal swelling in this assay guarantees an objective parameter, which enables the investigator to determine the damaging effects of test materials very precisely. This is in contrast to the conventional Draize rabbit test, which uses subjective gross measurements only. In combination with the measurement of corneal opacity and fluorescein retention, though assessed by subjective observation, but being very accurately measured by the use of the slit-lamp microscope (see Figures), a reliable evaluation of the eye irritation potential of test materials can be achieved. In their latest updates of the guidelines on Eye Irritancy Testing, both the EC and the OECD (Organisation for the Economic Co-operation and Development) allow for the use of alternative ex vivo/in vitro test systems for pre-screening or identification of severe eye irritants, in order to reduce animal use and suffering.

Furthermore, the CEET test is one of two organotypic in vitro assays accepted by ECVAM (European Centre for the Validation of Alternative Methods) in 2007 as partial replacement for the rabbit eye test to be used as screening tests for the identification of substances as ocular corrosives and severe eye irritants in a tiered testing strategy as part of a weight-of-evidence approach.

The results of the eye irritation tests are in the following text.

Skin irritation test: 3D skin model

A 3D skin model is a viable reconstituted human epidermis derived from human keratinocytes which in turn are derived from cosmetic surgery or circumcisions. The human origin of the test system itself therefore holds another considerable advantage compared to other animal models.

In August 2007, ESAC (European Scientific Advisory Committee) recommended the use of in vitro reconstructed human skin models for in vitro skin irritation testing. Since then, a prediction model based on a set of two parameters (viability and IL-1 alpha release) is considered to be state-of-the-art. The test is exclusively used for the prediction of irritating (I) or non irritating (NI). The multiple endpoint analysis (MEA) on Cimcool products includes histological examination and additionally determination of LDH release refines the prediction model tremendously. However, regulatory acceptance is still under discussion by the authorities.

In total, 27 products were tested undiluted; four products were also tested as a 5 % aqueous solution; results are shown opposite.

Azan-staining and hematoxylin / eosin (H&E) histology

Determination of quantitative IL-1 alpha release using an ELISA (Enzyme-Linked ImmunoSorbent Assay) technique
Results
In total Cimcool performed CEET eye irritation tests on 34 products and 3D skin irritation tests on 27 products; all at 100% concentration. Nearly all products are considered non-irritating; i.e. they don’t require labelling as R36* and/or R38**.

Exceptions include a mineral oil containing product which is considered an eye irritant. The skin compatibility, however, is good. Apparently, the chemistry used to give this type of product the required performance (including phenoxy propanol) contributes to the eye irritation properties.

The other four products considered skin/eye irritants include true synthetic, alkanolamine borate free, products. These products are highly concentrated and are consequently used at a mix of 2.5 to 5%. Therefore, although the product concentrate is irritating, these products in use are considered acceptable.

*R36 is the European Union’s definition for irritating to the eyes (substances and preparations which, when applied to the eyes of the animal, cause significant ocular lesions which occur within 72 hours after exposure and which persist for at least 24 hours).

**R38 is the European Union’s definition for irritating to skin (substances and preparations which cause significant inflammation of the skin which persists for at least 24 hours after exposure period of up to four hours determined on the rabbit according to the cutaneous irritation test method cited in Annex V.

These findings of the new 3D skin tests are completely in line with the company’s many years of experience with the previous tests. Over the years Cimcool has tested about 60 products using the TEWL test and 16 using the BUS test.

Experience with eye irritation is limited since recent alternatives to animal (rabbit) tests are just becoming more accepted. Additionally, eye contact should be avoided with both product concentrate and ‘in use’ product (because metal fines will be present in ‘used’ MWF fluids): the use of safety goggles (glasses) and any other relevant personal safety equipment is recommended.

Conclusions
Within the metalworking industry skin irritation is a generally occurring problem. Although the total influence of metalworking fluids is not fully understood it is now commonly accepted that wet working contributes significantly to skin irritation. Optimum working conditions, including a skin protection plan, will limit skin irritation.

For more than 40 years Cimcool has performed skin irritation tests to exclude metalworking fluids from being a significant contributor to skin irritation, always using the latest available technology.

With the recently completed state-of-the-art 3D skin and CEET eye irritation tests Cimcool not only has information on the irritating properties of the products in use: but also has the correct information on its safety data sheet about skin/eye irritation thereby fulfilling REACh and GHS requirements. In addition, because of the large scale investigations, Cimcool can extrapolate the data to other products. Last, but not least, it continues to provide information to the Engineering and Development (E+D) department to aid its goal of making completely skin compatible metalworking fluids.

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The competitive nature of the hydraulics market has created a trend of increasing power outputs and at the same time smaller fluid reservoirs. What are the consequences? The operating temperatures of hydraulic fluids used in these systems are significantly higher, leading to greater risks of oxidation and thermal degradation of the additives in the fluid. Varnish, the result of that degradation, can result in unplanned downtime, higher maintenance costs and lower profitability.

Over time, varnish build up can increase the friction inside the valves, especially those with fine tolerances such as servo and proportional types, where this phenomenon can be especially troublesome. Varnish buildup may cause servo valves to stick in an open position. The impact of sticking valves on the hydraulic system can be impaired responsiveness and reduced oil flow, which results in overall loss of efficiency and increase in maintenance costs.

What is varnish and how does it form? As oil ages, fluid degradation is caused by oxidation, thermal decomposition and the natural process of additive consumption. Additives - performance-enhancing chemicals - are consumed over the life of the fluid. Degradation byproducts increase as the oil ages, eventually forming varnish.

Since varnish is polar, it is attracted to metal surfaces such as servo valves. Varnish starts as a sticky, soft residue. The sticky nature of this material allows it to attract wear debris, resulting in the formation of a sandpaper-like surface. Eventually, the soft, sticky material transitions to a hard lacquer that can be very difficult to remove.

But, how does that varnish harm equipment? Oil that has been oxidised generally doesn’t lubricate very well. The result can be reduced oil flow, plugged filters, plugged valves, higher friction, poor heat transfer, and elevated operating temperature. Because varnish acts as an insulator, cooling capacity can be diminished.

On top of that, varnish shortens the lives of equipment components such as valves, filters, pumps, bearings and seals. What’s the bottom line? Hydraulic equipment performance suffers.

For example, in high-performance vane pumps, varnish adhering to the vanes can cause the vane to stick in the rotor slot. The consequences are increased noise, decreased volumetric and mechanical efficiency, increased energy consumption, side plate scuffing, rotary seal damage and possible bearing damage. Are there solutions for varnish? Electrostatic filtration systems can remove contaminants, but these systems don’t deal with varnish formation causes, tend to be expensive and can be susceptible to water contamination. Another is the commonly accepted practice for end users to routinely change or clean servo valves in hydraulic equipment to keep their systems running. One new valve can cost $3000 US, and the cost to clean and refurbish a valve can be about $2000 US. And don’t forget to add on the labour costs and the lost production costs of shutting down the equipment.

An ideal solution is using a hydraulic fluid that does not deposit varnish on surfaces. Fluids are now available that incorporate additive chemistry that reacts with the precursors of varnish, minimising the formation of tenacious, hard films on system hardware.

Laboratory testing demonstrates the keep-clean feature of fluids using this new technology. In industry-accepted pump tests, fluids containing many other additive technologies show varnish formation within 500 hours of operation. In the same pump tests, there was no evidence of varnish formation on system surfaces after 1,000 hours of use with fluids containing the new additive technology.

Fluids containing the new technology are particularly suited to hydraulic applications where high temperatures - mobile equipment, plastic injection molding machines, glass transfer systems, heavy presses, etc. - can be problematic and compromise the oil’s life. These fluids also are suitable for equipment owners who want to extend the life of their oil and their equipment, including valves, filters and pumps.

Today’s hydraulic fluids are being subjected to increasingly tough operating conditions. Demands to raise production at the same time as oil volume is decreasing emphasize the need for high-quality hydraulic fluids. The new varnish-reducing additive chemistry is the perfect partner for hydraulic fluids used in those harsher operating conditions.

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