Cutting Fluids and Skin Protection

Innovative models for assessing efficacy in development and practice
1. Introduction

In the metal processing industry, repeated contact with process chemicals, including cutting fluids, can cause occupational diseases of the skin. In the past, a variety of strategies have been pursued by the industry and by manufacturers of process chemicals and skin protection products. In view of the special significance of this for jobs in the metal sector, the responsible workers’ compensation funds [Berufsgenossenschaften (BG)] have launched numerous plant-specific and general initiatives.

Workplaces today are often designed so that contact with process chemicals is avoided completely or as far as possible. Metal cutting, for instance, is often carried out in highly automated machining centers, in which long-term contact with metalworking fluids no longer occurs.

In recent years, there have been various efforts aimed at improving the skin-compatibility of process chemicals. In water-miscible cutting fluids, for example, dermatologically problematic ingredients have been reduced or eliminated, resulting in products with demonstrably improved compatibility.

If employees suffer changes to the skin of their hands, lower arms or face under operational conditions, this is often erroneously said to be the result of an allergy. In fact, a wide variety of mechanisms can produce the clinical picture of an occupational skin disease:

- in the short term, when hazardous substances, contaminated process chemicals or incorrect use cause acute, clinically observable skin reactions;

- in the medium to long term, when the skin is repeatedly exposed over a prolonged period of time to fluids exhibiting an intrinsically very low irritative potential in single cases of contact. This will eventually lead to chronic skin disorders (cumulative toxic contact dermatitis);

- immunological reactions can cause an allergic contact dermatitis in persons who are hypersensitive to certain substances (allergens/sensitizers). The occurrence of allergic contact dermatitis depends on the disposition of the individual and generally cannot be predicted. However, it is often preceded by chronic skin damage, which weakens the barrier function and allows a critical increase in penetration by allergens to occur.

Education about activities that stress the skin and the general use of skin protection products have proved effective in preventing and avoiding the occurrence of occupational skin diseases. This is demonstrated by the clearly improved situation in plants where there is an established skin protection concept that covers cleansing and caring for the affected skin areas as well as targeted skin protection measures.

Besides this empirical knowledge, in recent times there have been a number of initiatives aimed at scientifically verifying and quantifying the efficacy of skin protection products.

Modern physiological methods and experimental studies on volunteers are used to provide proofs of efficacy, as for other types of cosmetics. Furthermore, in recent years in-vitro methods have been developed to the point where they can be used for a wide range of applications. A currently relevant example is the BUS model (isolated perfused bovine udder skin model; Kietzmann et al. 1993), which is used to study the skin compatibility...
of construction chemicals, process chemicals, cosmetics and cosmetic ingredients, and to demonstrate the efficacy of skin protection products.

The purpose of this brochure is to provide concise information concerning important issues in skin protection and the development and use of modern cutting fluids.

The brochure first introduces the following themes:
- structure and protective function of the skin;
- general aspects of skin protection;
- dermatological risks associated with metal processing;
- optimization of process chemicals and occupational skin protection measures.

The results of Henkel's and Herwe's own studies are then presented. They concern:
- the optimization of the skin compatibility of cutting fluids during their development;
- testing the skin compatibility of cutting fluids in use;
- the efficacy of skin protection products against irritative metalworking fluids sampled from metalworking plants.
2. The skin

2.1 GENERAL

The skin effectively seals off the inside of the body from the outside world, and is primarily designed as a protective organ. This is why it has its own independent metabolism and, depending on function, a very varied appearance. The surface of the skin has an area of 1 to 2 square meters. The skin accounts for about 7% of total body weight and is therefore the largest human organ. Moreover, it is in many ways closely and visibly connected with the psyche.

In detail, the skin is made up of four structural compartments (see Figures 1 and 2), whose function requires a high degree of integrity:

- the external epidermal layer with keratinocytes as the prevailing cell type, and the corneocytes that form the surface (see 2.2);
- the basal membrane (see 2.3);
- the dermal layer (see 2.4);
- the hypodermal layer (see 2.5).

The dermal and hypodermal layers account for more than 90% of the total volume of the skin.

2.2 EPIDERMIS

The cells of the basal layer (stratum basale) have bulbous protuberances which lie on the basal membrane. They produce daughter cells by division. These keratinocytes take three to four weeks to differentiate on their journey to the surface of the skin.

In the overlying prickle cell layer (stratum spinosum), the cells are very closely connected by spiny protuberances, which stabilize the viable epidermis. The thickness of this layer is variable. It is 3 to 4 cells thick in the thin skin of the eyelids and 10 to 20 cells thick in the skin of the inside of the hand (area used to grasp objects) or the soles of the feet.

The granular layer (stratum granulosum) is the last layer of cells beneath the corneocytes. It contains precursors of keratin in the form of large and conspicuous granules, as well as the horny layer lipids that subsequently act as intercellular cement. As in the case of the prickle cell layer, the thickness of the granular layer is not the same all over the body, being only 1 or 2 cells thick in the skin of the eyelids and up to 5 cells thick in the skin of the palm.

In the horny layer (stratum corneum), the typical cellular structures such as the cell nucleus are no longer recognizable and the cells are completely keratinized. The cells in the lower and middle sections of the horny layer are very firmly and closely bonded to each other by cementing substances and special structures (desmosomes). The closer the cells are to the skin surface, the weaker this bonding becomes. Individual cells or groups of cells are continuously shed from the surface in the form of scales. The structure and thickness of the horny layer at any part of the body depend on the local frictional stresses to which the skin is subjected.
2.1 HEADLINE

The epidermis contains other cells, with special functions, between the keratinocytes. The most important of these are the melanocytes and the Langerhans cells. Both of these cell types possess long cell branches and protuberances, which enable them to penetrate specific epidermal regions. The melanocytes produce the pigment melanin, ready for transfer to the keratinocytes. The dendritic Langerhans cells, which account for about 8% of all epidermis cells, belong to the immune system. They are the body’s immunological outposts, and are in close contact, through the lymphatic vessels, with the lymph nodes and other immunological organs.

2.3 BASAL MEMBRANE

The basal membrane is embedded between the epidermis and the dermis. It is attached to the epidermis by bulbous protuberances from the basal cells and to the dermis by anchor-like collagen structures. The interaction between both skin compartments is regulated through this close connection. The basal membrane is penetrated by branches of the cutaneous nerves.

Where the epidermis has to be firmly attached to the dermis, as in the palm of the hand, the degree of folding of the basal membrane increases in proportion to the degree of frictional stressing.

2.4 DERMIS (PAPILLARY, RETICULAR)

 Immediately below the basal membrane is the loose structure of the papillary dermis with more nerve endings, the lymphatic vessels and the capillaries of the densely organized system of blood vessels that serves the epidermis, which has no blood vessels of its own. Further down is the thicker reticular dermis, with dense collagen bundles, elastic fibers and a relatively low degree of vascular organization. The degree of firmness of the skin depends on the thickness of the connective tissue of the reticular dermis.

2.5 HYPODERMIS

The hypodermis is the innermost skin layer. It lies below the hair papillae and consists of connective and fatty tissue. It is a key element of the body’s temperature regulation system.

2.6 SKIN APPENDAGES

The skin appendages include hairs, sebaceous and sweat glands, and nails. They are not uniformly distributed over the skin but are grouped very specifically according to the region of the body.
2.7 PROTECTIVE FUNCTION

The protective function of the skin is performed almost exclusively by the hydrolipid film and the keratinized cell layers of the epidermis.

The term ‘penetration’ is used when topically applied substances pass through the horny layer toward the inner epidermis. The term ‘permeation’ is used when a substance crosses the line of separation (the basal membrane) between epidermis and dermis. ‘Absorption’ is incorporation in the systemic circulation. The possible binding and absorption zones in the epidermis and dermis are also shown, with the possibility of metabolizing foreign substances.

Penetration into and through the hair follicle and sweat gland (shunt diffusion) is a special case. It used to be thought that the hair follicles have a subordinate role, as the hair follicle orifices occupy only approximately 0.1% of the skin surface. Today there is some debate as to whether, immediately after contact, follicular penetration plays a greater role than interfollicular. In the context treated here, process chemicals and skin protection, the outer follicle zones can be said to have a reservoir function.

Penetration and permeation into the viable epidermis, dermis and hypodermis is dependent on the reservoir and barrier functions of the horny layer (stratum corneum). The horny layer reservoir contains the substances available for further penetration or permeation. The horny-layer-substance phase builds up anew depending on the formulation and the duration and intensity of the exposure. Anatomically, it precedes the barrier, although there is no sharp boundary within the horny layer.

Figure 1: Diagram of the four skin compartments, showing their thickness (µm), and the penetration paths (Structure and dynamics of the skin barrier, in: Skin Barrier – Principles of Percutaneous Absorption; printed with the permission of Verlag S. Karger, Basel)
The hydrolipid film (less than 1 µm thick, also referred to as the protective acid layer) is composed of the secretions of the sebaceous and sweat glands and the horny layer lipids (cement). Depending on the volume of sweat, a water-in-oil (W/O) or an oil-in-water emulsion (O/W) is formed. The hydrolipid film has a certain anti-microbial potential and can act as a buffer against alkaline and acidic substances. Its pH lies between 4.2 and 5.6. It is therefore the basis for the weakly acidic reaction of skin’s surface.

The hydrolipid film is directly adjacent to the horny layer. This is about 10-20 µm thick and consists of densely packed layers (10-20) of corneocytes. The horny layer provides gradually increasing protection against penetrating substances and physical influences, depending on the extent of the reservoir and barrier functions. At the same time it protects the body against water and electrolyte loss, by reducing the water content of the cells from about 85% to 15% within a few micrometers. The horny layer also has a pH delimiting function, as the pH in the granular cell layer is 7.4 while a slightly acidic environment prevails on the surface of the skin (pH approx. 5.4).

The horny layer in its totality is not, however, an absolute barrier, as, under physiological conditions, it allows water to pass through to the outside and topically applied substances to permeate through it into the deeper layers of the skin. Lipophilic substances follow the intercellular penetration path (between the corneocytes), while hydrophilic ones follow the transcellular path (through the keratinized corneocytes). Orifices formed by skin appendages such as hairs, sebaceous glands and sweat glands offer additional penetration paths.

As a result of the method of preparation, the horny layer, in which the reservoir and barrier functions are localized, is shown here as a loose agglomeration of flat, nucleus-free cells. The differentiation between the deeper, ‘firmer’ horny layer (stratum compactum) and the surface layer (stratum disjunctum) is not particularly distinct.

The significance of an intact horny layer is reflected in a comparison of the relative thickness of the horny layer (10-20 µm), epidermis (100-150 µm) and dermis (1000-1200 µm). The close relationship between the epidermis and the dermis is clear, with connective tissue and vessels (blood and lymphatic vessels) sometimes closer to the skin surface than the corresponding epidermal areas and thus more accessible to external influences. The boundary and contact zone (basal membrane) between the epidermis and the dermis is therefore – depending on age – larger than the actual external skin surface.
3. General aspects of skin protection

3.1 DEFINITION AND SIGNIFICANCE OF OCCUPATIONAL SKIN DISEASES

Annex 1 of the Occupational Diseases Ordinance [Berufskrankheiten-Verordnung (BKV)] defines occupational skin diseases as follows (ref. BK 5101):

**BK 5101:** Serious or recurring skin diseases that require the sufferer to desist from all activities that were responsible for, or could be responsible for, the appearance, aggravation or reappearance of the disease.

This definition contains the main prerequisites for recognition as an occupational disease.

For many years, diseases that conform to the BK 5101 definition formed one of the most frequently occurring groups of occupational diseases. In the period from 1994 to 1998, a total of 392,490 reports of suspected cases of occupational disease were processed, of which 136,527 were confirmed. Of the confirmed cases, 40,424 (29.6%) were skin diseases (see Table 1).

<table>
<thead>
<tr>
<th>All industrial occupational groups</th>
<th>Turners (occupational group 221)</th>
<th>Metal grinders (occupational group 225)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All occupational diseases</td>
<td>136,527</td>
<td>1,624</td>
</tr>
<tr>
<td>Skin diseases (BK 5101)</td>
<td>40,424</td>
<td>824</td>
</tr>
<tr>
<td>Percentage</td>
<td>29.6%</td>
<td>50.7%</td>
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<td></td>
<td></td>
<td>43.2%</td>
</tr>
</tbody>
</table>

Source: BG statistics

Turners and metal grinders are numerically the most significant of the 24 occupational groups that fall under the category ‘metal producers/metalworkers.’ In these 2 occupational groups, the proportion of confirmed cases of skin disease relative to all confirmed cases was higher than the average for all industrial and craft occupational groups. They accounted for between 40 and 50% of all occupational diseases, although the absolute number of cases of skin disease was relatively low.

The data collected in recent years indicate that – partly due to changes in the job market – most skin diseases are now reported in the service industry: Some 50% of confirmed occupational diseases as defined in BK 5101 occur in the health service (see Figure 3), with the metal sector in second place with a much lower proportion of 11-17%. Comparable numbers of cases are also registered in the construction or building sector.
Irrespective of shifts in the figures, occupational skin diseases remain an economic and social problem throughout the entire field of work. Besides the costs to the public (around 150 to 160 million euros annually for pensions, rehabilitation measures and retraining), the effects on the lives of the sufferers also have to be considered. They may be unable to carry out their previous tasks and may lose their job or even become unfit to work at all.

A look at the causes of skin diseases in the metal sector (see Figure 4) shows that, alongside oils and greases and industrial rubber products and metals, cutting fluids in particular play a role. According to a publication of the Association of the Metalworkers’ Compensation Funds (Arbeitsgemeinschaft der Metallberufsgenossenschaften), they are the main cause of 37% of the examined cases.
3.2 TYPES OF OCCUPATIONAL SKIN DISEASES

Occupational skin diseases usually affect the hands and forearms, although other areas (e.g. face, lower extremities) may also be involved.

3.2.1 Cumulative toxic contact dermatitis

The most common form of occupational skin disease is cumulative toxic contact dermatitis, or CTCD (German: Abnutzungsdermatose), also referred to as toxic-degenerative eczema, chronic degenerative eczema, cumulative subtoxic contact dermatitis, or chronic irritative contact dermatitis. Dermatitis (eczema) is defined as a non-infectious inflammatory reaction of the epidermis and dermis. CTCD is caused by the cumulative effect of contact with the same or different types of sub-irritative influences. Since CTCD also depends on the exposure conditions, personal factors (atopy) and activities outside of work, it often appears in the workplace only as isolated cases. Nevertheless, this is the main form of occupational skin disease, with an estimated share of 40% of total cases.

When it occurs, CTCD is caused by repeated skin contact with non-acute toxic concentrations of noxae (Latin: noxa, meaning harmful substance) over a long period of time. It is not induced by occasional skin contacts with these noxae.

A typical cause of CTCD is continuous contact with aqueous substances in the workplace. These may be products and preparations such as cleaners and alkalis, cutting fluids admixed with water, or hand cleansers or disinfectants. Such substances can substantially deplete the surface hydrolipid film and cause increased swelling of the horny layer cells, thus reducing its resistance to wear (frictional and chemical influences). The skin’s moisture content is also reduced, causing it to become too dry. Moreover, lipids are also leached out of the horny layer (defatting; see 2.2). Alkaline process chemicals and products can change the slightly acidic environment of the horny layer and impair the regeneration of the affected skin.

CTCD may develop over a period of months or years. At first only subclinical changes occur, e.g. transepidermal water loss (TEWL). The first visible changes then appear; the skin surface becomes dry, cracked and largely inelastic, and typical symptoms of CTCD gradually manifest themselves (e.g. itching, reddening, scaling).

This development is shown graphically in the Malten diagram (Figure 5). In example A, the incidents of harmful skin exposure are subtoxic and are widely enough separated in time to allow complete regeneration to occur. The skin does not become diseased and does not exhibit any typical symptoms. In example B, there is no interval between the incidents. Regeneration cannot occur, so that the full range of symptoms can gradually develop, depending on the individual factors.
Subclinical damage to the horny layer, e.g. as a consequence of corneocyte swelling due to repeated permeation of moisture into the skin, keratin denaturation by toxic components or drying out of the skin (increased TEWL), upsets the balance of the barrier and reservoir functions and therefore causes considerable changes in the penetration and absorption properties. Incomplete regeneration enables foreign substances – fat-soluble rather than water-soluble – to penetrate more easily and reach the living cells of the epidermis, the basal membrane and the hypodermis with the cells of the fibrovascular tissue. This triggers cellular pre-inflammatory and inflammatory reactions, which weaken the barrier function still more and cause the full clinical picture of cumulative toxic contact dermatitis to develop.

3.2.2 Acute toxic contact dermatitis

Acute toxic contact dermatitis (ATCD) occurs more rarely than the chronic form. This is an immediate skin reaction (e.g. blistering) triggered by a single contact with a noxa. The noxa might be an acid, an alkali, an oxidizing agent or an extremely defatting fluid. Improper use, or contaminated or otherwise modified process chemicals may also trigger acute skin reactions. In this case a large number of employees may be affected, i.e. the skin problems may develop epidemic proportions.

3.2.3 Allergic contact dermatitis

Allergic contact dermatitis (ACT), elicited by sensitization through previous skin contact with a substance or a structurally similar compound, still plays a significant role. The degree and frequency of sensitization depend on the immunogenity (allergenic potential) and concentration of the allergen, the duration and frequency of the contacts, and the disposition of the individual. It is known that the probability of sensitization is significantly increased by any impairment of the skin barrier – e.g. by cumulative toxic contact dermatitis or its preliminary stages. In such cases the penetration of allergens into the living skin layers is facilitated to such an extent that smaller dosages than those assessed in allergen tests on healthy skin can induce sensitization or trigger a reaction.
Sensitization to, for example, biocides may also be induced by repeated skin contacts with products outside of
the workplace. The same is true of all allergic reactions to certain metals, such as cobalt, chromium and nickel.

In contrast to cumulative and acute toxic contact dermatitis, in cases of allergic dermatitis the skin does not
acquire a degree of resistance to the trigger substance once it has healed. The allergic reaction is triggered by
each new contact with the allergen.

3.3 PREVENTION OF OCCUPATIONAL SKIN DISEASES

In principle, the following measures can be taken to prevent the occurrence of occupational skin diseases:
• reduction of exposure by changing work procedures (organizational measures) and equipment
  (technical measures);
• reduction of exposure by changing or improving process chemicals;
• use of protective clothing (gloves, etc.) or skin protection products (skincare ointments, emulsions, etc.);
• complementary and supplementary occupational health measures.

Avoidance of factors that are harmful to the skin in the workplace is highly effective. This has been demon-
strated successfully in the construction industry, with the use of low-chromate cements, and in the hairdress-

ing sector, where glyceryl monothioglycolate is no longer used in permanent waving products. These measures
alone brought about a clear reduction in the occurrence of skin diseases in these occupational groups.

The use of personal protection is necessary and mandatory for the purpose of avoiding contact with acutely
toxic substances (also systemically toxic or carcinogenic ones) when it is not possible to completely ban their
use or prevent all exposure to them.

Skin protection ointments or emulsions (personal skin protection) are generally used when employees repeat-
edly come into contact with non-acute toxic concentrations of certain process chemicals and are unable, or are
not permitted, to wear protective clothing for various reasons (e.g. diminished sense of touch, or rotating
machine parts).

The most important reason for using a skin protection product is therefore to avoid contracting cumulative
toxic contact dermatitis or the onset of its preliminary stages and thus also to reduce the probability of sensi-
tization.

Skin protection products also have an important role to play in minimizing the risk of inducing dermatitis when han-
dling process chemicals that acquire toxic properties when they undergo changes during use, e.g. when they are han-
dled wrongly or when work procedures are inefficiently organized. Some examples taken from the metal sector are
described in section 4.4.

Organizational measures can serve as a supplementary and complementary instrument, e.g. in the context of
occupational disease prevention programs. Such measures include the collection of plant-specific data (e.g.
concerning the dermatological health of employees, workplace analysis, process chemicals analysis) and advi-
sory activities. Both approaches form the basis for effective implementation of the abovementioned package of measures. As another example, new employees who will have to carry out activities that may impair the health of the skin could be subjected to an initial dermatological examination.

3.4 COMPONENTS OF PERSONAL SKIN PROTECTION

Personal skin protection measures at the workplace are made up of 3 inseparable components:

• hand protection (creams, which should be applied before and during work);
• skin cleansing (cleansers, depending on the degree of soiling);
• skin care (creams, which should be applied after work).

3.4.1 Skin protection

The first rule of skin protection is to use the correct product for the workplace substance with which the skin comes into contact. Various types of skin protection products are described in section 3.5.

Such products must be applied carefully and comprehensively, especially to ‘forgotten’ areas, such as the sides of the hands, the nail bed and the groove of the nail bed, and between the fingers. To ensure they provide optimal protection at the workplace, skin protection products should be applied before starting work, after frictional stressing, and always after cleansing the skin.

3.4.2 Cleansing the skin

The skin should be cleansed gently in a manner appropriate to the degree of soiling. Unfortunately, this is often neglected.

Some routine industrial jobs are very dirty (e.g. due to graphite, metal dust, paint, adhesives, used oils and greases), so that workers need to clean their hands as many as 20 times each day. This means that the skin quickly loses much of its natural lipid and moisture content. Repeated cleansing of the hands in these workplaces is an important skin-stress factor, which should be given serious attention.

Since each cleansing operation stresses the skin, a mild skin cleanser should always be used wherever possible. Although products with powerful cleansing action now exhibit relatively good skin-compatibility (due to the inclusion of mild surfactants, solubilizers, gentle abrasives and emollients), they should be used carefully and sparingly, and only to remove heavy soiling. If such products are not available at the workplace, products that are very harmful to the skin (e.g. hand brushes, solvents) are often used to remove heavy soiling. It is therefore often better to provide several skin cleansers with different levels of cleansing power, e.g. a product with and a product without abrasives.

An important aspect of hand cleansing is the consistent use of a skin protection product before starting work. The product saturates the skin, so that soil cannot adhere as strongly and the hands can therefore be cleansed more easily. This may then allow a product with less cleansing power to be used.
Alongside the correct choice of cleansing product, the proper use of the product is also important. A small amount of hand cleanser should be spread over the dry hands and the soil should be removed using just a little water. The hands should then be thoroughly rinsed in order to remove any surfactant residues, before being carefully dried, without excessive frictional stressing (rubbing).

3.4.3 Skin care

Skin care, as the third component of skin protection at the workplace, should promote the regeneration of stressed skin after work. The objective is to return the skin to its natural condition outside of working hours. Section 3.5.5 describes how skin care products work.

3.5 HOW SKIN PROTECTION AND SKIN CARE PRODUCTS WORK

Skin protection products function in a complex manner. On the one hand they can form an almost impenetrable barrier to process chemicals (barrier creams), while on the other hand they supply and saturate the horny layer with protective ingredients. In addition, the targeted use of substances such as tanning agents is possible; these react with proteins in the horny layer, thereby strengthening it and providing more protection.

The efficacy of skin protection products depends not only on their ingredients but also on factors such as emulsion type, fineness of distribution, and interaction between ingredients. These factors determine the spreading capacity and absorption characteristics of the product. Since skin protection products can only be completely effective if they are accepted cosmetically and do not hinder users as they work, a pleasant fragrance and ease of handling are of great importance, next to optimized formulation.

3.5.1 Products that protect the skin against straight process chemicals

Products that provide protection against straight process chemicals (e.g. oils, straight cutting fluids, greases, nonpolar solvents) have the task of preventing these substances from leaching lipids out of the intercellular zones of the horny layer and from penetrating into deeper layers of the skin.

These products, which have little or no emollient content, are usually based on water-soluble O/W dispersions. Emulsifiers with a relatively high HLB (hydrophilic-lipophilic balance) value, i.e. a relatively high polarity and low fat-solubility, are therefore used.

Film-forming polymers, such as medium-chain polyvinyl alcohol or polyethylene glycols, are often included as barrier substances. They are able to form strongly adhering films that are resistant to many lipophilic substances.

Certain inorganic solids are used as supporting ingredients. These include talcum (a water-containing aluminum silicate with excellent skin adhesion properties) and zinc oxide with an astringent action.
If the skin protection product is intended to significantly reinforce the subsequent cleansing of heavily soiled skin (metal dust, graphite, oil, grease), emulsifiers with a high HLB value or surfactants are additionally incorporated. Since the latter should have good skin compatibility, weakly acidic, mild surfactants (e.g. disodium lauryl sulfosuccinate) are preferred to alkaline surfactants (soaps).

3.5.2 Products that protect the skin against water-miscible process chemicals

In workplaces where there is contact with water-miscible substances (cutting fluids admixed with water, salt solutions, aqueous cleaners, disinfectants, dilute acids and alkalis, construction materials such as lime or cement), strongly hydrophobic products with a high lipid content are usually preferred. They prevent swelling of the horny layer cells and the associated leaching out of moisture-binding substances. The depletion of horny layer lipids (e.g. by washing active substances or emulsifiers) is also reduced.

As vaseline-type pure hydrocarbon products are extremely greasy on the skin, only emulsified products with correspondingly superior cosmetic properties are now used. Besides the classic W/O bases, W/O/W and O/W types are also marketed.

The protective components are lipophilic substances and, in many cases, hydrocarbon mixtures, such as medicinal white oil and vaseline. In appropriate formulations, these form a water-resistant protective film and also have an occlusive action; such products are therefore also used to provide protection against dry skin, e.g. in very cold conditions.

Special emulsifiers with a low HLB value (e.g. glyceryl oleate) are used to prepare the W/O emulsions, which are then often stabilized with magnesium sulfate.

Weakly acidic buffering (pH 5.5 - 6.5) is useful in products intended to provide protection against alkalis and alkaline construction materials, as this reinforces the skin’s ability to neutralize alkalis.

3.5.3 Products that protect the skin against a variety of process chemicals

Special skin protection products are available for employees who come into contact with a variety of process chemicals. Such products can be used against both water-miscible and straight process chemicals, but are often less effective than specific skin protection products.

The products are based on O/W emulsions and often have a high solids content. The active ingredients include film formers and, in some cases, astringents (tanning agents, zinc oxide), which strengthen the horny layer and thus provide protection against aqueous process chemicals. Waxes and wax-like substances (beeswax, long-chain fatty acids, fatty alcohols) are also resistant to aqueous fluids and many water-insoluble fluids.
3.5.4 Products that provide skin protection when occlusive protective clothing is worn and when the skin is subjected to physical stresses

In many fields of work, occlusive protective gloves are increasingly being worn as protection against various chemical and physical stresses. The use of enclosed, fully automatic processing machines means that gloves can also be worn in the metalcutting sector, as there is no longer any risk of contact with moving parts.

Although protective clothing eliminates direct contact with process chemicals, problems may be encountered when it is worn for long periods. The exclusion of air causes a build-up of heat and moisture (profuse perspiration), resulting in an increase in pH, softening of the horny layer (maceration) and, after a period of time, microbial decomposition of perspiration.

Astringents and antiperspirants such as aluminum chlorohydrate and various synthetic or vegetable tanning agents are used as effective components to combat these skin phenomena. These substances inhibit perspiration or strengthen the horny layer by reacting with the protein matrix of the corneocytes. They have an antimicrobial action and this reduces sweat decomposition.

The action of the astringents in strengthening the horny layer means that they can be used against purely frictional stresses (e.g. skin contact with sand, rough surfaces, wire wool, glass fibers). The corresponding products are based on lipid-free gels or O/W emulsions, as an excessively high lipid content can reduce the impermeability of certain types of gloves (e.g. latex).

3.5.5 How skin care products work

The task of skin care products is to support the regeneration of stressed or damaged skin. After work and the subsequent hand cleansing, the skin must, above all, be provided with lipids and humectants.

Strongly emollient W/O products, O/W creams or O/W lotions may be used, depending on the stresses to which the skin is exposed and the skin type. The care effects depend not only on the solids content but above all on the type and composition of the emollients. Many of the simple products that are available contain only paraffin hydrocarbons (liquid paraffin, vaseline, etc.).

Lipids with an ester structure have been found to have good absorption, spreading and skincare properties. Natural vegetable oils (e.g. avocado oil, almond oil, coconut oil, etc.), some of which contain non-saponifying substances (sterols, etc.), are of importance here. Synthetic oils based on glycerine esters (e.g. MCT oils), waxes (beeswax, jojoba wax) and other fatty acid esters (isopropyl myristate, octyl dodecanol, etc.) should also be mentioned.

Due to work stress and hand cleansing, not only lipids but also certain moisture-binding substances, referred to as NMFs (natural moisturizing factors), which occur naturally in the spaces between the cells of the horny layer, are partially depleted. These are low-molecular substances such as sodium lactate, urea, uric acid, hydroxycarboxylates, etc. These substances, together with other humectants (e.g. glycerine), are incorporated in skin care products for the purpose of reducing any further moisture loss.
Alongside the lipids and moisture regulators, the products sometimes contain other care additives. Some of these protect the cell walls (e.g. antioxidants such as tocopherol and its derivatives), while others promote cell regeneration (e.g. allantoin).

3.6 PROOFS OF THE EFFICACY OF SKIN PROTECTION AND SKIN CARE PRODUCTS

Under the definition in section 4 of the German Food and Commodities Act [Lebensmittel- und Bedarfsgegenständege setz (LMBG)], skin protection, skin cleansing and skin care products are classified as cosmetic products and are therefore subject to the corresponding European and national legislation. According to the 6th amendment to the EU Cosmetics Directive, the claimed efficacy of skin protection and skin care products must also be demonstrated.

Although it is difficult to provide the required proofs for all types and preparation forms of process chemicals, there are a number of approaches that can be used to shed light on the suitability of skin protection products in various situations. Certain guidelines on occupational skin protection products are already available from scientific associations (e.g. Society for Dermopharmacy).

However, there are no generally accepted standard test methods in this area. Standard methods only exist for products intended to provide protection against UV radiation.

There are basically two types of methods for determining the efficacy of skin protection products.

3.6.1 In-vivo methods

The product is assessed on the basis of the reactions observed on the skin of volunteers after repeated application of standard irritants (repetitive open irritation test, ROIT). The difference between the reaction of the skin to irritants with or without prior application of the product is an indicator of the product’s protective effect.

Frequently used standard irritants include the following:

- for water-miscible process chemicals: sodium lauryl sulfate (SDS, SLS), lactic acid, sodium hydroxide;
- for straight process chemicals: toluene, N-hexane.

Possible test parameters include:

- visible skin reactions (reddening, swelling, scaling);
- measurable parameters such as transepidermal water loss (TEWL), cutaneous blood flow (BFV) or corneal skin moisture.

The use of in-vivo methods is subject to strict ethical and legal restrictions. The use of process chemicals (freshly prepared or sampled after industrial use) or health-endangering standard irritants in the test may pose ethical and legal problems. Studies based on animal tests are out of the question on legal grounds, as skin protection products are, by definition, cosmetics.
3.6.2 In-vitro methods

Basically, in-vitro methods are free of ethical and legal restrictions and in this regard are easier to assess than in-vivo methods. In addition, they often have the advantage that the tests can be performed faster, more economically and more repeatably, i.e. free from influencing factors relating to individual volunteers. The limits of in-vitro methods are to be found in their lack of comparability with in-vivo methods and their inadequate transferability to everyday working situations, i.e. their lack of relevance to practical reality.

A distinction is drawn between physical and biological test methods. The solubility of formulations can be checked very easily by Suskind's method (a physical method). Objects (e.g. slides, spoon handles) coated with skin protection ointments can be immersed and agitated in a process chemical. If the skin protection coating dissolves partly or fully, the product is not suitable as a protection against this process chemical. Other physical approaches are based on the possibility of testing the barrier and buffer properties of skin protection products. The measurements are carried out on special carrier films in permeation measurement cells with the help of indicator reactions and photometry.

For cell or skin models based on biological principles, the degree of metabolization of foreign substances is important, as is the presence of a functional horny layer. This is because the harmful effects of the standard noxae used and the efficacy of the tested skin protection product are both reflected in the horny layer.

The conditions mentioned above are found in isolated perfused organs in connection with the skin as the target organ. Examples of perfused organ models include porcine limbs, porcine ears and bovine udders. The most frequently used and in many respects the most advanced test model is the BUS (bovine udder skin) model (Kietzmann et al., 1993; SIMRED GmbH), which was developed to study the absorption capacity of drugs, among other things. Since then, numerous studies have been carried out into, for example, the penetration of cosmetic active ingredients and other constituents under leave-on and rinse-off conditions, and cellular reactions after topical application (open/occlusive) of pharmaceuticals, cosmetics, disinfectants, construction and process chemicals. The cell reaction chain includes the rapidly triggered changes in the arachidonic acid metabolism (e.g. prostaglandin E₂ concentrations) and the final irreversible cell damage. A design for a two-stage test for studying the efficacy of skin protection products was developed on this experimental basis, incorporating invasive measurement methods (see 6.3).
4. OPERATING SEQUENCES IN THE METALWORKING SECTOR

A variety of fluids are employed to support work processes in the metalworking sector. They facilitate the machining of the workpieces or serve to chemically modify or clean their surfaces.

Figure 6 shows a typical sequence of metalworking processes.

Machining may also be preceded by cleaning and/or treatment with corrosion inhibitors. Processing chemicals of widely differing composition are used for these purposes. This brochure is mainly concerned with metal cutting operations (cutting, turning, milling, grinding, drilling, honing) and thus with cutting fluids.

Figure 7 shows a cutting operation.
4.2 TYPES OF CUTTING FLUIDS

Cutting fluids are preparations (mixtures) that are used in the metalworking sector to cool and lubricate tools and workpieces. They also serve to rinse off and carry away the chips. A distinction is made between various types of cutting fluid on the basis of solubility and emulsion type:

Figure 8: Types of cutting fluids


Straight cutting fluids are applied directly without added water. Water-miscible cutting fluids are mixed with water to produce either emulsions (disperse systems) or solutions. Depending on the emulsifier system, the resulting emulsions may be either hydrophilic (oil-in-water = O/W) or lipophilic (water-in-oil = W/O). The most frequently used cutting fluids are those that can be mixed with water to form O/W emulsions.

4.3 COMPOSITION OF CUTTING FLUIDS AND POTENTIAL RISKS ASSOCIATED WITH THEIR COMPONENTS

As well as being able to perform their primary task, cutting fluids must satisfy a number of secondary requirements. In the case of water-miscible cutting fluids, these include:

- good miscibility with water over a wide range of water hardness;
- good stability (storage stability, emulsion stability, microbiological stability);
- corrosion inhibition (machines, tools, workpieces);
- low foaming;
- absence of aggression toward non-metallic parts (seals, cable sheaths, etc.);
- compatibility with metalworking fluids in the upstream and downstream processing steps;
- environmental compatibility;
- non-hazardous to health (skin, respiratory tract).
Cutting fluids contain a number of additives to enable them to satisfy these requirements. Some of these – at least, viewed in isolation – are potentially harmful to the skin. Typical components are listed in Table 2.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Examples</th>
<th>Task</th>
<th>Potential risks to skin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base materials</td>
<td>Mineral, partly synthetic and fully synthetic oils</td>
<td>Lubrication</td>
<td>Skin defatting, PAH (benzo[a]pyrene) from mineral oil</td>
</tr>
<tr>
<td>Polar additives</td>
<td>Natural fats, oils, synthetic esters</td>
<td>Improved adhesion of lubricating film</td>
<td>Skin defatting</td>
</tr>
<tr>
<td>EP additives (extreme pressure additives)</td>
<td>Organic sulfur, phosphorus and chlorine compounds</td>
<td>Protection against wear</td>
<td>Skin defatting, sensitization and skin irritation due to degradation products</td>
</tr>
<tr>
<td>Corrosion inhibiting additives</td>
<td>Amines, sulfonates, organic boron compounds, tall oil fatty acids</td>
<td>Protection of metals against oxidation</td>
<td>Sensitization</td>
</tr>
<tr>
<td>Anti-aging additives</td>
<td>Organic sulfides, zinc dithiophosphates, aromatic amines</td>
<td>Prevention of reactions in cutting fluid (especially oxidation)</td>
<td>Sensitization</td>
</tr>
<tr>
<td>Solid lubricants</td>
<td>Graphite, molybdenum sulfides, ammonium molybdates</td>
<td>Improved lubrication</td>
<td>Soiling</td>
</tr>
<tr>
<td>Emulsifiers</td>
<td>Surfactants, petroleum sulfonates, alkali and amine soaps</td>
<td>Emulsion formation and stabilization</td>
<td>Skin defatting</td>
</tr>
<tr>
<td>Defoamers</td>
<td>Silicone polymers, tributylphosphate</td>
<td>Prevention of foaming</td>
<td>Skin defatting</td>
</tr>
<tr>
<td>Biocides</td>
<td>Phenol derivatives, formaldehyde releasers, isothiazolinones, etc.</td>
<td>Prevention of excessive microbial growth</td>
<td>Sensitization</td>
</tr>
</tbody>
</table>

(Source: Bagschik U., Boveleth W., Gebert J., Rabente T., Sonnenschein G. (2001), modified)
The potential risk associated with individual ingredients or groups of ingredients depends on the formulation and concentration, and it does not necessarily follow that there is any risk associated with the total formulation or the application solution (see also 6.1.2). The finished products may exhibit good overall skin compatibility. Whenever possible, modern, skin-compatible products are formulated without components that are associated with potential problems (see 5.1).

4.3.1 Risks associated with water-miscible cutting fluids

The potential risk associated with all water-miscible cutting fluids derives from the presence of what is assumed to be a harmless component, namely water. Long-term contact with aqueous fluids (wet work occupation), especially in association with surfactants and a high pH, causes the corneocytes to swell and the horny layer (stratum corneum) to lose its lipid content. This can cause cumulative toxic contact dermatitis (see 3.2.1). The high pH of cutting fluids impairs the acid layer of the skin and thus impairs its defenses against microorganisms.

Skin problems are often suffered by persons who regularly come into contact with aqueous fluids at work and in their free time. Water alone can damage the living epidermis cells simply by repeatedly penetrating into the horny layer, as every housewife knows. In everyday working life, not only cutting fluids but also surface cleaning, hand cleansing and hand disinfection are of importance (see 3.4).

4.3.2 Risks associated with straight cutting fluids

Skin changes are also observed when straight cutting fluids are used. They do not cause the horny layer to swell, nor do they influence the pH of the skin, but they can harm the skin by chronic defatting or through the additives they contain (e.g. antioxidants), depending on the type and concentration. Reactions with the sebaceous gland or its efferent duct or the hair shaft cannot be predicted with any certainty, but in sensitive persons they can lead to oil acne.

4.4 Risks associated with external modification of cutting fluids

Water-miscible and straight cutting fluids may pose an additional risk during use, due to external contamination and material changes. Acute toxic skin reactions in particular are usually attributable to such changes under application conditions.

4.4.1 Nitrosamine formation

N-nitrosamines are potent carcinogens. They are formed when secondary amines react with nitrite or other nitrosating substances (e.g. dinitrogen trioxide). The quantitative significance of cancers caused by nitrosamine contact in association with the use of cutting fluids is, however, very slight. From 1988 to mid 1994 only 35 cases were reported to the Central Federation of the Workers’ Compensation Funds [Hauptverband der gewerblichen Berufsgenossenschaften (HVBG)] and only 5 of these were confirmed.
Today there is virtually no risk of nitrosamine formation in cutting fluids. This is a result of the ban on the use of reaction partners (nitrite, secondary amines) in TRGS 611 (see 4.5). Small quantities of the starting substances can, however, be introduced into the cycle by entrainment (preparation water, foreign products, impurities) or microbial changes.

4.4.2 Other external chemical and physical changes

One important source of risk associated with used cutting fluids is the formation of very fine metal dust from the workpiece or tool as a result of abrasion. Since mixtures of water and cutting fluids contain surfactants, oil and tiny metal particles are held in suspension and may cause microlesions in the horny layer.

In this context, metal ions may also accumulate in cutting fluids. It has already been demonstrated that allergic skin diseases can be triggered by contact with cutting fluids that contain cobalt or nickel (e.g. during tool grinding). However, comparative studies of apprentices before they start their working lives and employees who suffer from skin diseases and have therefore been permanently transferred to a dry working environment have shown that metal allergies have no quantitative significance in relation to skin diseases.

Moreover, degradation processes (pyrolysis, oxidation) can cause secondary products to be formed while cutting fluids are being used. In this way, biologically active components may also accumulate in cutting fluids.

The increase in concentration of cutting fluids in the cycle and on machine, tool and skin surfaces due to evaporation is a general problem. The resulting excessively high concentrations of components may also pose a risk to the skin. Under certain conditions, ‘secondary concentrates’ with a cutting fluid content of up to 50% may build up within spraying range of machine tools.

4.4.3 Microbiological changes and preservation

Microorganisms can be introduced into cutting fluid systems through the preparation water, soil, dust and food residues and insufficiently cleaned pipes, or through skin contact in general.

The organic components of cutting fluids admixed with water are in principle a nutrient substrate for microorganisms. Under the prevailing conditions (e.g. elevated temperature), microbial growth is promoted by ‘dead’ and inaccessible spaces and rough surfaces in the system (in pipes, collection tanks and filtration systems). Certain microorganisms flourish in the absence of oxygen. Such anaerobic conditions are found in stagnant systems (e.g. lack of circulation at weekends, etc.) or under air-excluding surface oil layers (e.g. contamination by tramp oils).

Excessive microbial growth and the resulting changes (degradation, inversion or separation) in emulsions can cause technical problems (e.g. corrosion and tool wear) and hygienic problems (e.g. putrid odors due to sulfur compounds, bacterial and fungal action).
There may be also some health-endangering consequences:

- formation of sensitizing or skin-irritant degradation products;
- bacterial skin infections, e.g. inflammation around cuts;
- facilitation of nitrosamine formation through pH reduction and increased nitrite concentration.

Biocides are added to many products to inhibit the growth of microorganisms (see Table 2). The biocides are divided into formaldehyde releasers and non-releasers. The formaldehyde releasers are water-soluble and more effective against bacteria than against fungi. Non-formaldehyde-releasing products may be fat-soluble or water-soluble and are effective against both fungi and bacteria. The non-formaldehyde-releasing isothiazolinones are usually added to ensure continued preservation of the product during its service life. If biocides are formulated appropriately and used in the correct amounts, they will have no particular risk potential. The same or chemically similar products are also used to preserve cosmetics. The addition of excessive amounts or the use of biocides that are incompatible with the formulation can, however, cause skin problems (irritation, sensitization). This can happen when preserving agents are added at regular intervals, or as needed, for the purpose of ensuring continued product preservation.

4.5 LEGAL REGULATIONS APPLYING TO CUTTING FLUIDS

In view of the potential risks associated with cutting fluids, regulations and guidelines have been formulated by German and EU legislators, workers’ compensation funds, etc., which ban or limit the use of certain ingredients and regulate the handling of chemical substances in general. Table 3 shows the current regulations.

<table>
<thead>
<tr>
<th>Rules/section</th>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazardous Substances ordinance, section 4a</td>
<td>Categorization of component substances (if applicable, self-categorization by the manufacturer)</td>
</tr>
<tr>
<td>§ 14</td>
<td>Supply of a safety data sheet by the manufacturer (see also TRGS 220)</td>
</tr>
<tr>
<td>§ 15 Annex IV</td>
<td>Ban on nitrite and nitrosating component substances</td>
</tr>
<tr>
<td>§ 16</td>
<td>Duty of employers to identify risks associated with process chemicals and, if necessary, substitute them</td>
</tr>
<tr>
<td>§ 18</td>
<td>If applicable, conformity with threshold values in air (MAK [maximum workplace concentration], TRK [technical guide concentration], BAT [biological workplace tolerance value]); see also TRGS 402, 403, 900 and Bundesarbeitsblatt 3/96</td>
</tr>
<tr>
<td>TRGS 905</td>
<td>Categorization of certain components as carcinogenic, mutagenic or a danger to reproductive capability.</td>
</tr>
<tr>
<td>Rules/section</td>
<td>Contents</td>
</tr>
<tr>
<td>---------------</td>
<td>----------</td>
</tr>
<tr>
<td>TRGS 611</td>
<td>Restrictions on the use of, in particular, nitrite and secondary amines in water-miscible cutting fluids, due to the formation of N-nitrosamines. TRGS 611 specifies the application of TRGS 552.</td>
</tr>
<tr>
<td>TRGS 531</td>
<td>Protective measures with regard to risks to the skin when working in a wet environment</td>
</tr>
<tr>
<td>BG rule BGR 143 (formerly ZH 1/248)</td>
<td>Safety and health protection when handling cutting fluids. Advice for operational practice</td>
</tr>
<tr>
<td>VKIS-VSI-IGM - substance list for cutting fluids conforming to DIN 51385 for metalworking (compilation from various sources)</td>
<td>Demands on water-miscible/straight cutting fluids and additives: - list of banned substances; - list of substances and limiting values / concentration thresholds; - list of notifiable substances (relevant in the context of occupational health, toxicology or ecology); - list of notifiable substances (relevant in the context of process technology).</td>
</tr>
</tbody>
</table>
5. Measures for avoiding health risks in metalworking plants

The following measures for maintaining the health of the skin when handling process chemicals – and especially cutting fluids admixed with water – are partly of a conceptual and partly of an organizational nature. For the implementation of all measures, it is essential that all persons involved in the work processes should be provided with the necessary knowledge by means of training courses and operating instructions. A skin protection plan for metalworking plants is included here under 5.3. Occupational health measures are not described here in more detail (initial dermatological examinations to select employees, prevention programs, etc.; see 3.3).

5.1 OPTIMIZATION OF THE PROCESS CHEMICALS

In recent years, the manufacturers of process chemicals and the workers’ compensation funds have brought about enormous improvements in the health and environmental compatibility of workplace chemicals. Problematic process chemicals have been identified and either replaced or modified. Supporting educational programs have additionally helped to raise awareness.

The proportion of additives associated with skin and environmental problems has been deliberately minimized in modern products (e.g. core program of Henkel Technologies), which satisfy or more than satisfy the legal requirements (see 4.5). Optimized total formulations yield process chemicals with excellent skin compatibility, outstanding technical properties, and good environmental compatibility.

In the case of water-miscible cutting fluids, this can be achieved by:
- dispensing with components that are known to be associated with risks to health or the environment, e.g. secondary amines and chloroparaffins;
- excellent emulsion stability;
- balanced microbiological suitability;
- inclusion of a skin-compatible additive as a booster for EP applications (EP = extreme pressure);
- lowering the usual application concentrations.

The labeling of process chemicals in conformity with the Hazardous Substances Ordinance usually relates to concentrates and is done on the basis of the component substances. In this context, it is worth noting that none of the cutting fluid concentrates in Henkel Technologies’ core program has to be labeled with the risk phrase R38 (Irritating to skin).

Additional skin-compatibility studies (in-vivo and in-vitro) have been carried out on various cutting fluids (see Table 4). With the exception of the straight cutting fluids MULTAN® 201 and 233, these studies were carried out on emulsions in concentrations of 4 or 5% by volume.

The two skin-compatibility test methods applied in the studies differ in principle and in their procedure and evaluation. The COLIPA standard simple 24-hour patch test is carried out under occlusive conditions on volunteers. Evaluation starts 6 hours after the end of exposure and is carried out clinically, i.e. subjectively (reddening, swelling, scaling). An objective, quantitative determination of skin compatibility in the first minutes or hours of contact with the cutting fluid is not possible.
The in-vitro BUS test (see 6.1) is carried out under open conditions, with all the consequences in terms of an increase in concentration of the test substance due to evaporation, as also occurs in practice. The full-thickness skin biopsies (epidermis and dermis) are evaluated by means of biochemical measurement methods that reflect two key stages of the irritation mechanism. In this way, subclinical skin reactions are determined quantitatively and objectively immediately and during the first hours after contact with the cutting fluid, as shown in the Malten diagram (see Figure 5).

<table>
<thead>
<tr>
<th>MULTAN®</th>
<th>24h patch test* (volunteer study) in-vivo method</th>
<th>BUS model** (perfused udder skin) in-vitro method</th>
<th>Label R38 (Irritating to skin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97-10 D</td>
<td>R 9900636</td>
<td>assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>71-10</td>
<td>R 0000730</td>
<td>assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>77-70</td>
<td>R 0100640</td>
<td>not assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>60-1</td>
<td>R 0100981</td>
<td>not assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>21-60</td>
<td>R 0001006</td>
<td>not assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>70-40</td>
<td>R 0000513</td>
<td>assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>97-10 D /201</td>
<td>R 0000514</td>
<td>not assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>201 straight</td>
<td>R 9800654</td>
<td>assessed</td>
<td>Not required</td>
</tr>
<tr>
<td>233 straight</td>
<td>R 9800886</td>
<td>assessed</td>
<td>Not required</td>
</tr>
</tbody>
</table>

* Henkel Technologies, unpublished reports  ** SIMRED GmbH

The results of the different test methods indicate that the cutting fluids listed in Table 4 (4-5 vol.-% or undiluted) exhibit very good skin compatibility.

### 5.2 OPTIMIZATION OF THE WORK ENVIRONMENT AND WORK PROCEDURES

The work environment can be optimized by means of two packages of measures:

- reduction of skin contacts with process chemicals;
- regular checks and avoidance of unnecessary exogenous stresses on process chemicals and thus retention of their skin compatibility.

#### 5.2.1 Reduction of contacts

Process chemicals are designed and optimized to enable them to perform their function in the metalworking sector. Even if they have been demonstrated to be compatible with the skin, they do not exhibit the skincare properties that one expects from skincare products. As process chemicals can have a defatting effect over long periods of repeated contact, the duration of any contacts should be restricted to the essential minimum (see 4.3.1 and 4.3.2).
This can be achieved by:
• using fully automatic supply systems for processing machines
• enclosing the machines and interrupting the cutting fluid flow when they are opened;
• fitting suitable spray protection devices and air extraction systems;
• wearing protective gloves, which is not permissible when handling rotating machine parts;
• rapid, automated cleaning of processed workpieces.

5.2.2 Protecting process chemicals against external influences

During the service life of a cutting fluid, its good skin compatibility can be maintained by protecting the process chemical against excessive contamination, microbial loads and premature degradation. Key cutting fluid protection measures include:
• minimizing the entrainment of tramp oils, such as hydraulic oil, thus ensuring that surface oil layers do not form in reservoirs, as the anaerobic conditions under such layers encourage the growth of certain microorganisms;
• if necessary, removal of tramp oils with the help of skimmers, centrifuges, etc.
• if necessary, installation of pumps to circulate the cutting fluid when long idle periods occur, thus preventing the formation of oil layers and the creation of anaerobic conditions;
• ensuring that the volume of circulating fluid is sufficient to prevent high temperatures from being reached, as this can encourage excessive growth of microorganisms;
• optimization of the cutting fluid outflow and avoidance of rough surfaces and inaccessible spots in the system, in order to inhibit the formation and multiplication of colonies of microorganisms;
• minimization of soil entrainment from outside, e.g. by enclosure, avoidance of walkway grids over open systems;
• complete separation of solids, as far as possible (filter systems).

5.2.3 Operational checks, addition of preserving agents and replacement of cutting fluids

Besides these preventive technical care measures, constant monitoring of the quality of cutting fluids is essential. When necessary, they must be treated or replaced.

Operational checks of cutting fluids should include the measurement of the following parameters:
• concentration;
• nitrite content;
• pH;
• in certain cases, the microorganism count.

Fresh cutting fluid can be added to ensure continued preservation. If necessary, biocides can be added selectively for the same purpose. The addition of excessive amounts of biocide should be avoided.

If the emulsion is no longer fit for use, it must be completely or partly replaced. Defining fixed replacement intervals has proved to be operationally practical.
When fluids are replaced, the total circulation system must be thoroughly cleaned and disinfected. This is done with the help of system cleaners, which are added to the emulsion before the change is effected. When the emulsion has been run off, the system must be thoroughly rinsed.

### 5.3 PREPARATIVE SKIN PROTECTION AND SKIN CARE PLAN

It has been demonstrated that the use of preparative skin protection beneficially complements the measures described above (see 5.1, 5.2) in the metalworking sector.

Previous sections (see 3.5) describe the composition of skin protection products and the way in which they function. The following table shows in general, with examples, which skin protection products should be used for which process chemicals.

<table>
<thead>
<tr>
<th>Skin stress factors / process chemicals</th>
<th>Recommended skin protection product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Water-miscible (hydrophilic) process chemicals</strong>&lt;br&gt;O/W cutting fluid emulsions, cutting fluid solutions, aqueous corrosion inhibitors, phosphating solutions, aqueous cleaners</td>
<td>Herwesan Acqua or Herwesan Acqua Liquido</td>
</tr>
<tr>
<td><strong>2. Straight (lipophilic) process chemicals</strong>&lt;br&gt;Straight cutting fluids, W/O cutting fluid emulsions, stamping oils, drawing oils, deep-drawing oils, spark machining oils, cold cleaners</td>
<td>Herwesan Olio or Herwesan Olio Liquido</td>
</tr>
<tr>
<td><strong>3. Alternating process chemicals</strong>&lt;br&gt;Substances from 1. and 2. in alternating use</td>
<td>Herwesan Due or Herwesan Due Liquido</td>
</tr>
<tr>
<td><strong>4. Wearing occlusive gloves</strong>&lt;br&gt;(for long periods)</td>
<td>Herwe Emulsion</td>
</tr>
</tbody>
</table>

In the plant, the skin protection products for the particular application are documented in a skin protection plan. This is drawn up by the responsible supervisors and their advisors (safety officer, occupational physician, BG employee), or in cooperation with the manufacturer of the skin protection product. The skin protection plan also shows the appropriate hand cleansers and the skin care products to be used after work.
It may be worthwhile to draw up separate skin protection plans for each process chemical that may stress the skin, so that individual employees have a better overview. An example of a skin protection plan, such as those found in the production zones of a metalworking plant, is shown below:

Figure 9: Example of a skin protection plan for a metalwork plant

SKIN PROTECTION PLAN

Technologies

<table>
<thead>
<tr>
<th>Skin-stress factor / workplace chemicals</th>
<th>SKIN PROTECTION before work</th>
<th>SKIN CLEANSING during and after work</th>
<th>SKIN CARE after work</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER-MISCIBLE PROCESS CHEMICALS</td>
<td>HERWESAN ACQUA</td>
<td>HERWE CURA</td>
<td></td>
</tr>
<tr>
<td>Dilute acids and alkalis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous cleaners</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water-miscible cutting fluids</td>
<td>HERWESAN ACQUA LIQUIDO</td>
<td>HERWE CURA</td>
<td></td>
</tr>
<tr>
<td>Moderate soiling</td>
<td>HERCULAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heavy soiling</td>
<td>HERCULAN FORTE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. Studies of the skin compatibility of cutting fluids and the efficacy of skin protection products

A cutting fluid must contain a variety of components if it is to satisfy all the demands made on it that derive from its interaction with man, machine and environment. General toxicological data on these components and additives, which are often only available in technical quality, are inadequate for the purpose of assessing local compatibility during product development and before use. Moreover, under operational conditions, degradation products, microorganisms and contamination by other process chemicals create a complicated volume of daughter substances, which may react with one another. A thorough knowledge of the application conditions gained from standardized studies before and during the use of cutting fluids enables further technical, organizational and personal protection measures to be taken on site, or provides the economic justification for a change of product.

6.1 BUS MODEL

The in-vitro isolated perfused bovine udder skin model (BUS model; development and implementation: SIMRED GmbH, 30938 Grossburgwedel, Germany) was used for the studies described below (see also 3.6.2 and 5.1). This method has been used by Henkel Technologies for a number of years in the context of, among other things, the development and application of cutting fluids. The BUS model has a functional horny layer and an active aerobic skin metabolism. With the help of full-thickness skin biopsies and biochemical methods, the model enables the development of local compatibility over defined exposure times to be monitored, compared with untreated skin, and assessed.

6.1.1 Test design and sampling

In the BUS test, the isolated bovine udder is perfused to ensure that the skin retains its viability for more than 8 hours. The experimental setup is shown in Figure 10. Further descriptions of the model and the test design can be found in the literature.
The test substance is applied topically to the udder (open or occluded application). Full-thickness skin biopsies (d=6mm; skin punch: Stiefel) are taken for the purpose of determining the biochemical parameters. Figure 11 shows a full-thickness biopsy and the histological section (right, H&E stain) through the udder skin (pigmented) with follicular and interfollicular areas (sampling technique: Histoshaver).

6.1.2 Skin reactions and measurement parameters in the BUS model

Skin reactions occur if the horny layer barrier is inadequate. This is the case when ingredients with irritation potential are liberated from the formulation and are able to penetrate the horny layer barrier or the epidermal cells. In the BUS model, the reaction of the skin cells is monitored invasively by means of several full-thickness skin biopsies taken at various intervals. The relationship between absorption, irritation potential and reaction is shown in Figure 12.
The cellular reaction over time after topical application of a formulation with irritation potential can be represented in the form of an exposure-effect curve (Figure 13 a).

Initially there is physiological activation of the tissue, followed by reversible structural changes in the cell membrane (cell irritancy). The final stage of the cellular reaction is irreversible cell damage (cytotoxicity). The course of the curve is influenced by the product used, the exposure time, and the quality of the barrier function of the skin.
The cellular reactions (Fig. 13b) are quantified in the BUS model by, among others, the biochemical determination of two different parameters:

- The degree of reversible cell irritancy is determined by measuring the concentration of prostaglandin E\(_2\) (ng PGE\(_2\)/µg DNA). Prostaglandins (eicosanoids) are part of the arachidonic acid metabolism and, as inflammation mediators, are one of the causes of skin reddening and swelling. The prostaglandin concentration in the tissue increases as the cell irritancy increases.

- The scope of the irreversible cell damage is determined by the methyl thiazol tetrazolium assay (MTT assay). This makes use of the mitochondrial function, measuring the proportion of still viable cells in comparison with untreated skin areas. Only functioning mitochondria in living cells are able to convert the added water-soluble MTT stain into water-insoluble formazan. As the degree of cell damage increases, the measured concentration of formazan therefore decreases (µg formazan/µg DNA).

The design of the BUS irritation test enables the kinetics of both parameters to be determined after 3 exposure periods (short term: 0.25 h and 1.0 h, long-term: 3.0 to 5.0 h) in untreated and treated skin, so that the skin compatibility of the test substance can be derived.

### 6.2 SYSTEMATIC STUDIES OF THE SKIN COMPATIBILITY OF CUTTING FLUIDS

Numerous authors have presented their results concerning the skin compatibility of cutting fluids and the methods used. Most of these data were obtained in in-vivo standard studies (volunteers, animal experiments) with fresh, unused cutting fluids. There is very little standardized laboratory data for used cutting fluids. Nevertheless, studies have shown that cutting fluids from plants with a high incidence of toxic contact dermatitis also cause the most skin irritation when used in experiments on volunteers with healthy skin (repetitive irritation test, RIT).

Studies carried out with the BUS model (SIMRED GmbH) using cutting fluids of the MULTAN® product range are outlined briefly below, together with the results (for details, see literature: Systematic in-vitro studies of the skin compatibility of cutting fluids; 2003, Pittermann W., Holtmann W., Kietzmann M.).
Table 6 shows a selection of the tested cutting fluids, with description, application concentration, and pH.

| Table 6: Examples of studied cutting fluids of the Henkel Technologies core program |
|-----------------------------------------------|--------|------|------|------|
| MULTAN®                                      | 97-10 D | 70-40 | 201  | 233  |
| Application concentration (vol.-%)           | 5%     | 4%   | 100% | 100% |
| pH                                           | 9.2    | 9.2  | Oil  | Oil  |
| High performance cutting fluids, boron-free  | X      | X    | X    | X    |
| Biocide, formaldehyde-releasing              | X      | X    | X    | X    |
| Mineral-oil-free, renewable raw materials   | X      | X    | X    | X    |
| High performance cutting fluids, boron-containing | X      | X    | X    | X    |
| Native oils, component of HD concept         | X      | X    | X    | X    |

6.2.1 Studies of the use of biocides in cutting fluids (water-miscible)

Biocides with a high degree of biological effectiveness are often incorporated in water-miscible cutting fluids. Their concentration may fluctuate during use. They are also topped up or added to the fluids to ensure their continued preservation.

The described test method was used to determine the irritation potential of various biocidal products at different application concentrations in MULTAN® 97-10 D. This assessment makes it possible to optimize the use of biocides in regard to the active ingredient and concentration.

6.2.2 Studies of application concentrations of cutting fluids (water-miscible)

Decisions with regard to the application concentration of water-miscible cutting fluids depend mainly on technical and economic objectives. With the BUS model, it is now possible to test skin compatibility relative to concentration.

Using MULTAN® 97-10 D, in-vitro tests were carried out with different, sometimes clearly excessive, concentrations. A broad, dermatologically favorable, concentration spectrum was determined for this product.
6.2.3 Studies of emulsifier systems in cutting fluids (water-miscible)

Emulsifier and surfactant systems are important components of cutting fluids. They enable the technically essential, finely dispersed emulsions with particle sizes of below 200 nm to be created. These components can have a biologically effective action when they interfere with the barrier function in the horny layer.

The MULTAN® 97-10 D and MULTAN® 70-40 cutting fluids differ in terms of their emulsifier systems, lubricant components and boron content. These two representative products were subjected to comparative studies.

The cutting fluids exhibited very good skin compatibility at application concentrations of 4 and 5% by volume and a pH of 9.2. No relevant differences were observed between the two products, i.e. the emulsifier system that was used was dermatologically neutral with regard to both fluids. The test models that were used (patch, BUS) indicated that both products can be rated as very good.

6.2.4 Studies of native oils in the MULTAN® HD concept

The main feature of the HD concept is the addition of products based on native oils of vegetable origin to improve technical performance.

The BUS irritation test was used to study straight MULTAN® 201 and MULTAN® 233, which are formulated on the basis of native oils.

Results of studies of MULTAN® 201 carried out on volunteers (24-hour patch test and other non-invasive methods) were already available. In general they document that the product exhibits very good skin compatibility. The results of the BUS test confirmed this for MULTAN® 201 and indicated that the skin compatibility of MULTAN® 233 is equally good. No fundamental differences between the 2 products could be measured.

6.3 STUDIES OF THE EFFICACY OF SKIN PROTECTION PRODUCTS

6.3.1 Preliminary remarks

If skin complaints are reported in a plant, the first thing to look at is the compatibility of the cutting fluids that are used there. Those responsible must also satisfy themselves that the skin protection plan was adhered to and/or that the protection potential of the available products is adequate under the prevailing conditions in the plant.

The following study arose from just such a recent case. In view of the unusually high incidence of cutting-fluid-related skin reactions (reddening/itching), the skin compatibility of the cutting fluid in use (competitor's product) and the efficacy of the required skin protection products in a metalworking plant were examined (see literature: Water-miscible cutting fluids, skin compatibility and skin protection - A case study; Pittermann W. and Geke J.).
6.3.2 BUS model (skin irritation and skin protection)

In past years, there has been intensive discussion about the issue of demonstrating the efficacy of skin protection products (see 3.6). The main focus of attention was on in-vivo studies of volunteers, in the form of irritation tests with induced repeated damage caused by standard noxae, such as SLS (hydrophilic) or toluene (lipophilic). At the present time there are no results available from standardized laboratory studies using fresh or used cutting fluids as noxae. Other in-vivo studies, such as animal experiments, cannot be carried out for ethical or legal reasons (see 3.6.1).

The BUS study design for determining skin irritation (see 6.1) was developed to test the efficacy of non-occlusively applied skin protection products and was validated in numerous projects (e.g., with commercial products that provide protection against lipophilic noxae) and publicized. The test design provides for the application of the noxae in parallel on untreated skin and on skin that has been pretreated with a skin protection product. This makes it possible to track and compare the level of the damage potential (noxa) and the protective effect of the skin protection product (SPP).

The used cutting fluid emulsion (application concentration approx. 5%) from the plant mentioned above was coded and used in 8 independent udder tests (SIMRED GmbH). It was applied non-occlusively (2 g/100 cm²). Another skin area was pretreated with the test skin protection product (Herwesan Acqua, Herwe GmbH; 2 g/100 cm²) for 15 minutes. After this exposure time the volatile components of the protective cream had evaporated and the horny layer was saturated, depending on the formulation. The first full-thickness skin biopsy was taken 15 minutes after the cutting fluid was first applied. The progress of the reaction in the skin treated with the protection product and the cutting fluid was compared with the nonpretreated skin and the untreated control area. This enabled the degree of damage caused by the cutting fluid and the protection potential of the cream to be evaluated in a standardized manner after 3 exposure times (0.25 h, 1.0 h and 5.0 h).

The validation of the test data for all exposure areas was carried out by means of variance analysis with a subsequent LSD test (LSD = least square difference) for multiple comparisons.

6.3.3 Result and summary

A standardized in-vitro BUS skin test was used to test the skin compatibility of a used commercially available cutting fluid in a concentration of approx. 5 vol.-% and the efficacy of a commercially available skin protection product (Herwesan Acqua, W/O emulsion) against this cutting fluid. Figure 14 (cytotoxicity) and Figure 15 (cell irritancy) each show 3 values per measurement time for the untreated skin, the skin area treated with used cutting fluid emulsion (CF emulsion), and the skin area pretreated with the SPP Herwesan Acqua and subsequently treated with cutting fluid. The results and assessment of the combined in-vitro study demonstrate that, when the test was carried out, the used CF emulsion was not skin-compatible and therefore must be regarded as the cause of the skin alterations observed among the workers.

After an exposure period of 15 minutes, no changes could yet be detected by biochemical means. The skin reaction (cell irritancy/cytotoxicity) started after an exposure period of 1.0 h. The strength and progress of the cellular reaction indicated skin-incompatibility after repeated contact, i.e., the clinical findings relating to plant
employees were experimentally confirmed. The pretreatment (15 minutes) with the skin protection product Herwesan Acqua reduced the skin reaction significantly. While cell damage (Figure 14) was slight and only occurred after a long period of exposure (5.0 h), the reduction in cell irritancy at the time of maximum concentration (1.0 h) was clear. The release of the inflammation mediator prostaglandin E₂, which is important for the further course of the skin reaction, was significantly reduced (Figure 15).

Results obtained with the MTT assay, showing the course of the cell damage. In contrast to the PGE₂ tissue concentration (Fig.15), a slight spontaneous increase in the number of damaged cells can be seen. The open application of the locally incompatible used CF emulsion appreciably reinforced this increase in irreversible cell damage and continued to do so until the end of the exposure period.

Pretreatment of the skin with Herwesan Acqua (SPP) for 15 minutes resulted in no changes in the cellular reaction in the first hour of exposure. After another 4 hours there was a slight difference between the pretreated and non-pretreated skin zones. This difference was not significant.
Results on the course of the cell irritancy. After open application of the used CF emulsion, the maximum increase in the PGE$_2$ tissue concentration was measured after an exposure period of 1 hour. After another 4 hours the increase proved to be reversible. In contrast, the concentration in the untreated control remained constant over 5 hours.

Pretreatment of the skin with Herwesan Acqua (SPP) for 15 minutes caused a statistically significant ($p \leq 0.01$) reduction in the maximum release of PGE$_2$ after 1.0 h. The subclinically skin-irritating action of the CF emulsion was therefore significantly suppressed.

Experience to date with the combined BUS model as a method of determining skin compatibility and demonstrating the efficacy of skin protection products indicates that the product Herwesan Acqua provides good protection against skin-endangering water-miscible cutting fluids under the conditions encountered in practice.
7. Summary

This brochure is intended to serve as a practical and informative guide to the complex subject of cutting fluids and skin protection. The main focus is on dermatological and regulatory aspects of the development and use of cutting fluids, and the special demands of skin protection in the workplace.

Numerous initiatives undertaken by the responsible workers’ compensation funds to raise awareness of the health and skin risks associated with cutting fluids have highlighted the importance of the management of process chemicals in the metalworking industry.

Other fundamental contributions have been and are being made by manufacturers, who aim to optimize cutting fluids during their development and application.

Concrete steps taken to minimize potential risks associated with water-miscible cutting fluids belonging to the core program of Henkel Technologies and to improve their compatibility are described. These include careful assessment of the raw materials used, avoiding the inclusion of skin-sensitizing and environmentally problematic substances and lowering the application concentration of the components.

These developments have resulted in top quality cutting fluid concentrates, which do not have to be labeled with the R38 risk phrase (Irritating to skin). The skin compatibility of application concentrations of 5.0% was tested by means of the COLIPA standard simple 24-hour patch test and in-vitro tests (BUS model, SIMRED GmbH). Both models yielded very favorable results.

Furthermore, the in-vitro skin model of the BUS system is a unique method allowing certain components of cutting fluids (e.g. biocides and emulsifiers) to be assessed, sometimes in different concentrations, to determine their aptness for inclusion in formulations. This biochemical method can also be used to carry out comparative studies of cutting fluids sampled from metalworking plants.

An important measure for avoiding the risks posed to the skin by process chemicals is the appropriate use of skin protection products. The possibility of using a valid in-vitro model was demonstrated using the special design of the BUS model for testing the efficacy of skin protection products. The efficacy of a skin protection product (Herwesan Acqua, Herwe GmbH) against irritative water-miscible cutting fluids used in practice was demonstrated.

Close scientific collaboration between manufacturers of cutting fluids and skin protection products offers new development opportunities. As a result of these efforts, customers can now benefit from a globally harmonized product concept in the metalworking sector.
8. Annexes

8.1 Abbreviations

ACT . . . . . . . . . . . . . . . . . Allergic contact dermatitis
ATCD . . . . . . . . . . . . . . . Acute toxic contact dermatitis
BFV . . . . . . . . . . . . . . . . . Blood flow velocity (cutaneous blood flow)
BKV . . . . . . . . . . . . . . . . Berufskrankheiten-Verordnung [Occupational Diseases Ordinance]
BG . . . . . . . . . . . . . . . . Berufsgenossenschaft [workers’ compensation fund]
BIA . . . . . . . . . . . . . . . . . Berufsgenossenschaftliches Institut für Arbeitssicherheit
[occupational safety institute of the workers’ compensation funds]
BK . . . . . . . . . . . . . . . . . Berufskrankheit [occupational disease]
BUS . . . . . . . . . . . . . . . . . Bovine udder skin
CF . . . . . . . . . . . . . . . . . . . . . Cutting fluid
COLIPA . . . . . . . . . . . . . European Cosmetic Toiletry and Perfumery Association
CTCD . . . . . . . . . . . . . . . Cumulative toxic contact dermatitis
EP . . . . . . . . . . . . . . . . . . Extreme pressure
H&E stain . . . . . . . . . . . . . Hematoxylin-eosin stain
HVBG . . . . . . . . . . . . . . . Hauptverband der Berufsgenossenschaften
[central federation of the workers’ compensation funds]
IGM . . . . . . . . . . . . . . . . . IG Metall [German metalworkers’ union]
LMBG . . . . . . . . . . . . . . . Lebensmittel- und Bedarfsgegenständegesetz [Food and Commodities Act]
LSD . . . . . . . . . . . . . . . . . Least significant difference
MCT . . . . . . . . . . . . . . . . . Medium chain triglyceride
MTT . . . . . . . . . . . . . . . . . Methyl thiazol tetrazolium assay
NMF . . . . . . . . . . . . . . . . . Natural moisturizing factor
O/W . . . . . . . . . . . . . . . . . Oil in water
PAH . . . . . . . . . . . . . . . . . Polycyclic aromatic hydrocarbons
PGE2 . . . . . . . . . . . . . . . . Prostaglandin E2
RIT . . . . . . . . . . . . . . . . . Repetitive irritation test
ROIT . . . . . . . . . . . . . . . . . Repetitive open irritation test
SLS . . . . . . . . . . . . . . . . . Sodium lauryl sulfate (sodium dodecyl sulfate)
SPP . . . . . . . . . . . . . . . . . Skin protection product
TEWL . . . . . . . . . . . . . . . . Transepidermal water loss
TRGS . . . . . . . . . . . . . . . . Technische Regel für Gefahrstoffe [technical regulations for hazardous substances]
W/O . . . . . . . . . . . . . . . . . Water in oil
ZIGUV . . . . . . . . . . . . . . . Zentrales Informationssystem der gesetzlichen Unfallversicherung
[central information system of the statutory accident insurers]

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