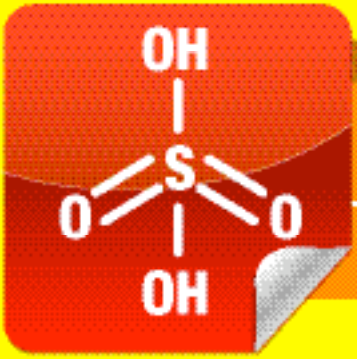


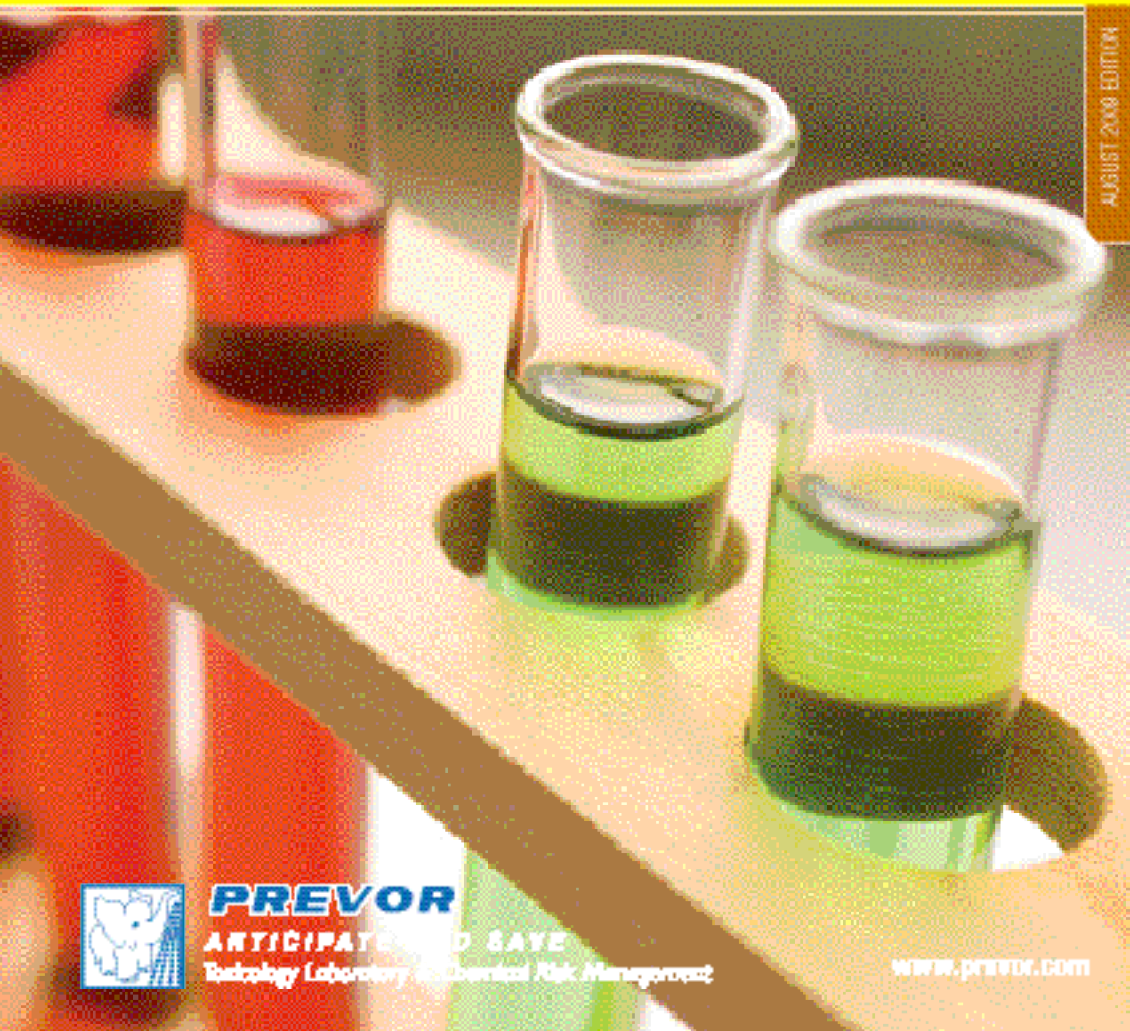
Product File

SULPHURIC ACID

CAS n° 7664-93-9

MANAGEMENT OF EYE AND SKIN CHEMICAL SPLASHES

AUGUST 2008 EDITION



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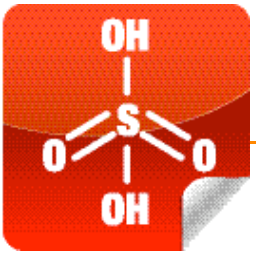


CONTENT

SULPHURIC ACID

MANAGEMENT OF EYE AND SKIN CHEMICAL SPLASHES

1. KEY POINTS

1.1. Background

Sulphuric acid has been known since the 8th century; two main processes are used today to produce it from sulphur dioxide:

- Catalysis
- A « contact » process

1.2. Names

Sulphuric acid (or sulfuric acid in USA) is also called:

- Sulphur trioxide (in its solid form CAS 7446-11-9)
- Oleum (anhydrous sulphuric acid saturated with CAS 8014-95-7 sulphur trioxide)
- Sulphuric acid (in its liquid aqueous form CAS 7664-93-9)
- Other name: vitriol or oil of vitriol (because of its glassy appearance).
- "Battery acid"
- Dihydrogen sulfate

ACIDE SULFURIQUE	
Molecular Formula	H_2SO_4 (aq)
Molar mass	98,08 $g.mol^{-1}$
CAS number	7664-93-9
EINECS number	231-639-5
ICSC number	0362
INRS[1]	FT n°30

1.3. Uses

Widely used in industry (approximately 150, 000, 000 tonnes a year worldwide), sulphuric acid is used in fertilizers, textiles, chemical synthesis, detergents, dyes and colouring, explosives, paper, accumulators, surface treatments and the petrochemical industry.
It is often the cause of chemical injuries[2] especially to the skin, the eyes, the respiratory tract and even the digestive tract.

1 - Institut National de Recherche et de Sécurité (The French National Research and Safety Institute)
2 - Flamminger A, Maibach H, Sulfuric Acid Burns (corrosion and acute irritation): evidence-based overview to management, Cut. Ocul. Tox, 2006, 25, 55-61

2. LABELLING

2.1. Level of danger according to concentration

- **EC classification in force until December 2010** for substances (until the end of June 2015 for mixtures):
  Product included in 19ème ATP[3].

SULPHURIC ACID	HAZARD SYMBOL	RISK PHRASES
Pure (substance)	C	R35
Concentration > or = to 15 %	C	R35
Concentration from 5 to 15 %	Xi	R36/38
Concentration from 0 to 4,99 %	-	-

Risk phrases are given at the end of the document

- **New labelling according to CLP[4] regulation, in force from December 2010** for substances (from the end of June 2015 for mixtures):

Danger !
H314 - Causes severe skin burns and eye damage

SULPHURIC ACID	CLASSIFICATION	HAZARD STATEMENT
Pure (substance)	Skin Corr 1A Skin Corrosion/irritation Hazard category 1A	H314
Concentration > or = to 15 %	Skin Corr 1A Skin Corrosion/irritation Hazard category 1A	H314
Concentration from 5 to 15 %	Skin Irrit 2 Corrosion/irritation Hazard category 2 Eye Irrit 2 Serious eye damage/eye irritation Hazard Category 2	H315 H319
Concentration from 0 to 4.99 %	-	-

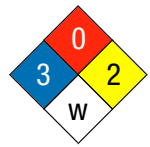
Hazard statements are given at the end of the document

3 - Adaptations to Technical Progress appendix 1 of the 1981 text see ECB
4 - Classification Labelling Packaging - Regulation 1272/2008/EC

2.2. Other classifications

UN Hazard Class : 8

In the United States[5] : **Code NFPA 704 :** H : 3
F : 0
R : 2
W : ---



3. CHEMICAL CHARACTERISTICS

A colourless liquid, more or less viscous depending on concentration; it has the capacity to form intermolecular hydrogen bonds.
Sulphuric acid is miscible with any amount of water with an exothermic reaction.

Molar mass	98,08 g.mol^{-1}
Boiling point	337°C
Melting point	10,31°C
Vapor pressure	Env 0,0001 mbar à 20°C
TLV[6]	1 mg/m^3 (VME) 1 mg/m^3 (TWA, NIOSH REL)[7] 1 mg/m^3 (TWA, OSHA PEL)[8]
Density (20°C)	1,8305 g/cm^3 (100 %) 1,8361 g/cm^3 (98 %) 1,3028 g/cm^3 (40 %) 1,1398 g/cm^3 (20 %)

Source: 87th edition of the Handbook of chemistry and physics - 2006-2007 edition

4. CORROSIVITY OF SULPHURIC ACID

4.1 - Chemical Mechanisms

Sulphuric acid corrosivity is due to a combination of four mechanisms:

- the acidity itself (production of H^+ ions),
- the dehydration caused by concentrated solutions,
- the heat released by exothermic reactions,
- the oxidizing nature of the chemical (concentrated or after warm-up).

4.1.1 Acidity

Sulphuric acid can release 2 H^+ ions successively in an aqueous solution:

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^- \quad pK_1 = -2$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \quad pK_2 = 2$$

Thus, for a molar concentration (1M), the corrosion potential of sulphuric acid is doubled.

5 - According to the International Chemical Safety Cards WHO IPSC ILO
6 - Threshold Limit Value
7 - Recommended Exposure Limit for the National Institute for Occupational Safety and Health
8 - Permissible Exposure Limit (for an 8 hour day as defined by the Occupational Safety Health Administration)

Acidity occurs also when sulphuric acid is used as a sulfonation agent:

$$2H_2SO_4 + H_2O \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

4.1.2 Dehydration Properties

Water-free, highly concentrated sulphuric acid solutions (above 95%) increase corrosivity. Indeed when it comes into contact with cellular biological fluids, the anhydrous product literally pumps out all the water, causing tissue necrosis.

4.1.3 Exothermy

In contact with water, sulphur trioxide produces sulphuric acid with heat release:

$$SO_3 + H_2O \overset{88\ kJ}{\rightleftharpoons} H_2SO_4$$

4.1.4 Oxidizing Properties

When concentrated and warmed up, sulphuric acid becomes an oxidant due to the following combination: $SO_4^{2-}/SO_{2(aq)}$ ($E_0 = 0,93$ V)

Source: 87th edition of the Handbook of chemistry and physics -2006-2007 edition

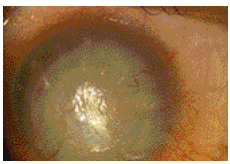
$$2H_2SO_4 + Cu \longrightarrow SO_{2(g)} + CuSO_4 + 2H_2O$$

4.2 - Chemical injuries due to sulphuric acid

When concentrated sulphuric acid comes into contact with the skin or the eyes, the pain is immediate. The short term effects on the skin are coagulation-induced necrosis (dark greeny black/brown). In the eyes, the cornea becomes opaque. In the event of inhalation, there is a risk of acute (more or less delayed) lung oedema.

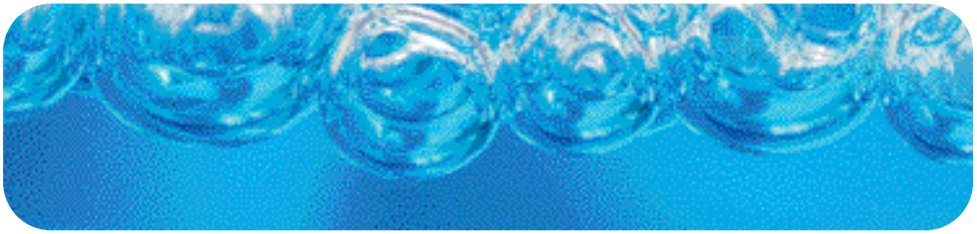
In the medium and long term, there is a risk of invalidating physical side effects in cases of skin injuries, including retractile fibrosis and / or keloid scarring.
In cases of chemical eye injuries, the risk of ocular perforation is significant. A chemical burn due to sulphuric acid can lead to definitive loss of the visual acuity.

Pictures from Dr Harold Merle



Pictures from Dr Harold Merle

Pictures from ASF



The severity of the chemical burn depends on concentration, which area of the body is affected and time of exposure.

Besides corrosivity, there is also the issue of carcinogenic consequences.

The IARC[9] classifies «aerosols and sulphuric acid and other strong inorganic acid mists » in group 1 (confirmed carcinogenic to humans). There is a risk of sinus, larynx and lung cancer. The mechanism involved could be related to chronic irritations due to work-related exposure.

5. MANAGING ASSOCIATED RISKS

> Collective and Personal Protection[10]

COLLECTIVE PROTECTION	• Work in a sealed environnment • Capturing emissions at their source
INDIVIDUAL PROTECTION	• Gloves (see table below) • Anti-acid face-shield or goggles • Masks with filtrating cartridge for occasional uses • Protective clothes (apron, boots, etc…)

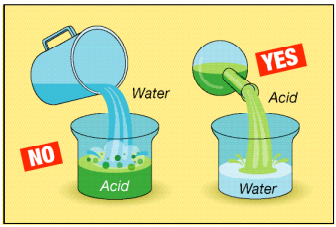
9 - International Agency for Research on Cancer
10 - Refer to full description in Toxicological Card n°30 of INRS

> Glove compatibility table

	LATEX	NEOPREN	NITRILE	VINYLE
CONCENTRATED SULPHURIC ACID	-	=	-	+
DILUTED SULPHURIC ACID	++	++	++	++

> Special Recommendations

- Availability of decontamination materials on all work stations.
- To be handled with care: never pour water into the acid. When dissolving or diluting, always add it slowly to the water, stirring constantly to avoid splashes and heating of substance.

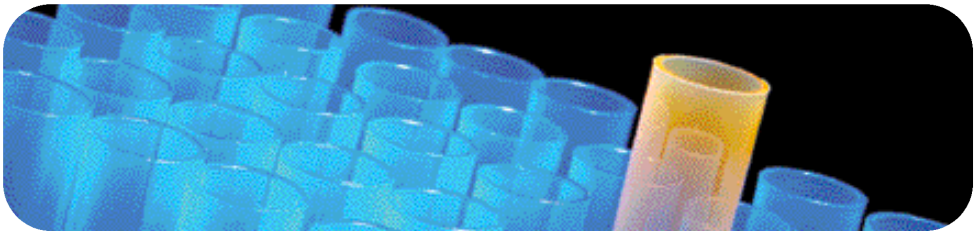


6. EMERGENCY RESPONSE TO SULPHURIC ACID SPLASH ON THE SITE OF THE ACCIDENT

The effectiveness of immediate washing of chemical splashes determines the subsequent outcome of the chemical accident. Splashes must be rinsed immediately after exposure to avoid or reduce severity of burns.
Ideally, one should seek to stop the substance's corrosive effect on the surface and prevent it from penetrating deeper into the skin or eye.

6.1. Evaluation of decontamination methods

Comparison of the standard method, tap water flushing, with an active washing method, Diphoterine® washing.



6.1.1. Rinsing with water

Water is polyvalent, it mechanically washes off the substance from the surface and at the same time dilutes it. Because of these properties at the surface of the tissue, water has been used as systematic and universal response. But water has its limitations. It must be applied immediately and in very large amounts. Despite an early washing with tap water, severe burns can appear, particularly in the case of concentrated corrosive substances. Thus this protocol can not be considered as constantly safe.

As we have seen, rinsing anhydrous solution splashes with water generates heat which can aggravate the chemical injury. However, mechanical rinsing and dilution can help to rapidly contain and eliminate heat evolution.

Since it has no effect on the corrosive potential of sulphuric acid, rinsing with water proves to be insufficient for high concentrations; this is illustrated by the following accident: walking down a corridor, a young female laboratory technician catches her open lab coat on a flask of concentrated sulphuric acid. The flask falls, breaks and spills splashing her leg that she rinses immediately with water. The injury heals then reoccurs over a course of several months.

6.1.2. Decontamination with Diphoterine®

In view of these problems, an active decontamination compound retains the wash-off effect of water while optimizing the decontamination process, thanks to the management of sulphuric acid's aggressive potential.

Washing with Diphoterine® is the answer to these criteria of effectiveness.

- its amphoteric properties ensure a rapid return to physiological pH values.
- Diphoterine® is a hypertonic solution that limits tissue penetration of the chemical. By creating a reverse flow, it can actually draw the chemical out of the tissues[11].
- Its multisite properties actually make it a highly effective decontamination method in all situations where sulphuric acid is used in combination with other irritant or corrosive chemicals.

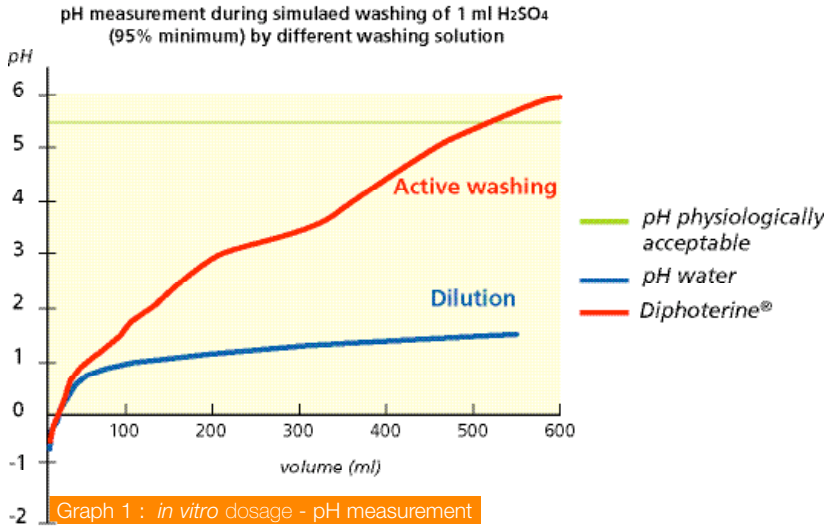
11 - Schrage NF, Rihawi R, Frentz M, Reim M, Akuttherapie von Augenverätzungen, Klin Monastbl Augenheilkd 2004, 221(4), 253-261

6.2 - Experimental evidence

The effectiveness of Diphoterine® was compared experimentally to a passive tap water rinsing method via an *in vitro* simulation of a 95% sulphuric acid splash.

The study showed the change in pH and in temperature of one millilitre of concentrated sulphuric acid in the presence of an increasing amount of water or Diphoterine®. During this static experiment, i.e. without the mechanical effect of dynamic rinsing, the chemical activity was measured in order to evaluate the effectiveness of the Diphoterine® rinsing, and more specifically, its amphoteric properties on a strong acid like sulphuric acid, *versus* water rinsing.

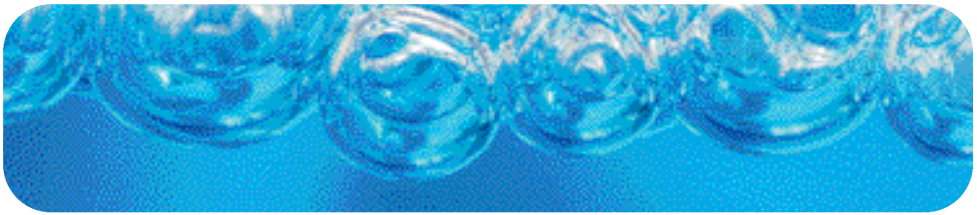
The sample tested corresponds to 5 drops of sulphuric acid at 95%.[12]



Graph 1 : *in vitro* dosage - pH measurement

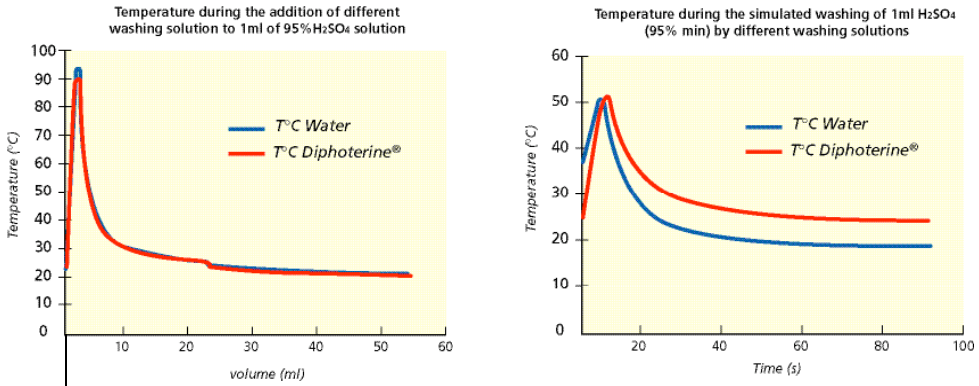
Graph 1 shows the simple dilution of sulphuric acid in water and, ex contrario, the effect of Diphoterine® on acidity with a faster return to an acceptable physiological pH level (>5.5) using a limited volume of 520 ml. It should be noted that for an equivalent amount of tap water, the pH (at approximately 1.5) remains very corrosive.

12 - On average, one drop is 20 µL. It is the maximum quantity which is able to remain on the corneal surface, whatever the quantity splashed, because of the blinking reflex as well as of the natural flow of the liquid.



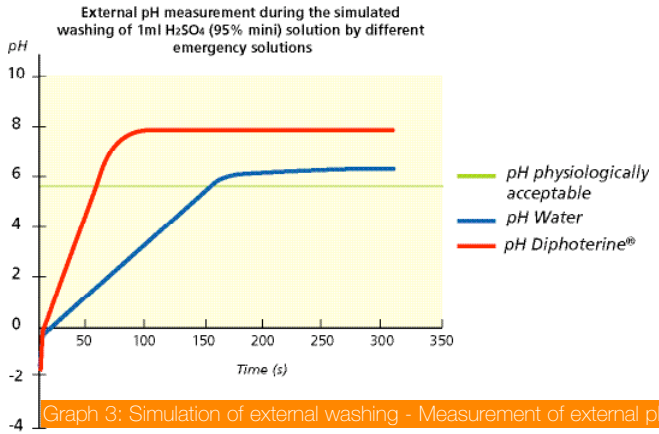
In the same experiment a solvation effect of sulphuric acid in water was observed, leading to heat release of approximatively 90°C (graph 2 - static simulation).

This effect rapidly diminishes during washing because the wash-off effect considerably reduced heat generation. The temperature, thanks to rinsing, only rises to 50°C, only for a few seconds, and rapidly returns to the temperature of the washing solution (graph 2 - simulation of external washing).

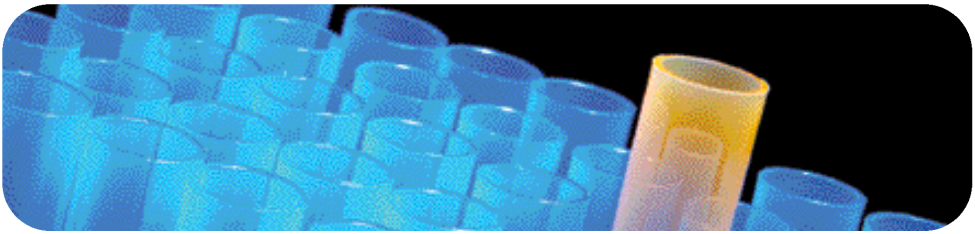


Graph 2: temperature measurement- static simulation - simulation of external washing

Graph 3 shows external pH changes over time. As in the static in vitro experiment, less Diphoterine® (59 ml versus 150 ml of tap water) is required to achieve lower physiological pH values and in two and a half times less time.



Graph 3: Simulation of external washing - Measurement of external pH



6.3 - Feedback on the use of Diphoterine®

The following paragraph lists some cases on the use of Diphoterine® to decontaminate eye or skin chemical splashes. This feedback shows that when Diphoterine® is applied immediately, it stops the action of sulphuric acid, thus avoiding or minimizing the development of chemical injuries. The other consequence is the absence of after-effects and no need for sick-leave. When Diphoterine® is used as a secondary response after rinsing with tap water, the chemical injury has already developed because water has failed to stop the action of the acid and has only diluted it on the surface tissues. Diphoterine® can then be used to stop any further development of the injury as it also acts on any acid that might have already penetrated the tissues.

February 1991 - La Quinoléine (Orgachim), Seine maritime - France

This accident was reported in 1991 by Dr. F. Bourlon, the company medical officer at the time. Two workers dismantling pipes were splashed from head to toe with 98% sulphuric acid. They were immediately undressed and washed with Diphoterine®, before being taken to hospital for further examination. They left hospital on the same day and did not require secondary care or sick-leave.

1995 – Metalleurop Weser Zink GmbH, Germany

Further to a technical fault during a routine test on a stock of acid, a technician was spattered on his face and neck with 96% sulphuric acid. Immediate rinsing with Diphoterine®, thus stopped the action of the acid, preventing burn injuries from appearing. The victim was able to go back to work immediately.

1994-1998 - Series of cases at Mannesmann, Germany

In a metal-working company, a series of chemical splashes occurred during the handling of acids and strong bases. The table below details eye and skin splashes from 20% sulphuric acid. All splashes were rinsed with Diphoterine® on the site of the accident and with Diphoterine® again in the company infirmary. The management of these splashes did neither require any secondary treatment nor sick-leave, and no sequelae did appear.

Age	Place on the body where the splash occurred	Secondary Care	Lost work time (days)	Sequellae	Circonstances of the splash
22	right eye	none	0	none	Pickling : hanging a chain
47	eye	none	0	none	Pickling : while filling an acid bath, ocular splash even ocular wearing protective goggles
46	right eye	none	1	none	Pickling : was splashed, in the eye with acid while cleaning
41	left eye	none	0	none	Pickling : while steam cleaning tiles, simultaneous splash of water and 20% sulphuric acid in the left eye
41	right eye	none	0	none	Was splashed while putting pipes in an acid bath
48	left eye	none	0	none	Was splashed while cleaning
25	right cheek	none	0	none	Was splashed with a chemical while opening a valve
26	torso	none	0	none	Pickling : was splashed with sulphuric acid while emptying a pipe
25	face	none	0	none	Pickling
27	right hand	none	0	none	Was splashed while handling acid

July 1999 - Knoll AG (BASF PHARMA), Germany

While collecting a sample, an operator was spattered on the cheek with a few drops of 96% sulphuric acid. The cheek immediately turned very dark red; the discoloration nearly entirely disappeared after being immediately rinsed with a Mini DAP of Diphoterine®. The doctor noted no residual redness on examination. A cream was applied to the operator's face and he was able to go back to work.

October 2004 - Teaching Hospital in Liège - Belgium

During a maintenance operation, a young man using a pipe clearing product was splashed with a corrosive product on a leg and a forearm. One of the ingredients of the clearing product was 90% sulphuric acid.
He was first rinsed with tap water, heightening the pain. Twenty minutes after the splash, the patient arrived in the casualties department of the hospital and was washed with a 200 ml Diphoterine® aerosol spray. This immediately reduced pain. Rinsing was continued. The worker was kept in observation and went back to work later that day, without needing sick-leave.

July 2005 - CMHI, Le Havre - France

While working on a incompletely emptied valve, a pipe operator was splashed on the face, neck and right ear with 98% sulphuric acid. Water rinsing was delayed (about 5 mn later) and a severe burn immediately developed. Diphoterine® was applied fifteen minutes later when the medical staff arrived on the site of the accident. After agreement of the occupational medicine officer and the intern in charge at the casualties department of the hospital, the patient continued to use Diphoterine® for a period of 48 hours as a pain-killer. After 72 hours, the oedema was no longer visible. The complete healing of this burn without scarring was obtained after 29 days, even though the initial severity of the facial burn would normally have indicated a longer development, requiring more significant secondary care and possibly a graft.

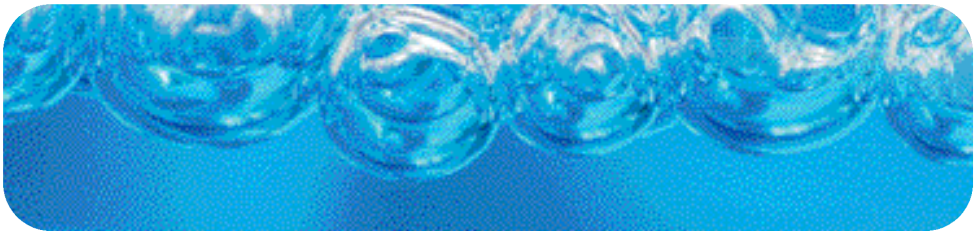
24h after the accident

72h after the accident

29 days after the accident

7. IN CONCLUSION, HOW SHOULD DIPHOTERINE® BE USED ?

Diphoterine® is a rinsing solution for emergency response to eye and skin chemical splashes. Thanks to its amphoteric properties, it acts directly on the irritant and corrosive potential of chemical agents. Because of its high osmolarity it stops any in-depth tissue penetration. This maximizes rinsing solution effectiveness, preventing or limiting corrosive lesions.



In cases of eye or skin splashes with sulphuric acid, we strongly recommend performing a rapid and prolonged washing with Diphoterine®.

In the event of an eye splash with sulphuric acid where the length of contact is less than 10 s, use a SIEW (50ml). In case of anhydrous sulphuric acid splash, we recommend to continuing the washing at the infirmary with 500ml of Diphoterine®.
For a length of contact between 10 and 60 seconds, use a 500 ml bottle or a 500 ml Portable Eyewash.
It is advised to complement washing with a 200 ml container of Afterwash II®.

In case of skin splashes and a length of contact less than 1 minute

- **for a smaller surface** (hand, neck...) use a 100 ml Micro DAP or a 200 ml mini DAP (face, arm, legs).
- **for a larger surface area**, use an Autonomous Portable Shower (DAP, 5 litres)

On the basis of our current findings on the optimization of washing conditions, Diphoterine® also proves to be effective for delayed washing (more than 60 seconds):

- **Eye splashes:** we recommend extending primary washing with a second 500ml bottle of Diphoterine®, ideally for 5 minutes. Washing more than 15 minutes is not necessary.
- **Skin splashes:** after the initial rinsing we recommend continuing the washing with one or several Diphoterine® containers for, ideally, 3 to 5 times the time of exposure to the chemical.

Rinsing should not be stopped because the pain is reduced. The entire container must be used.

In all cases, the injured person must be referred to a doctor to check skin or eye status and in the event of respiratory or digestive lesions.

8. DOCUMENTS AND REFERENCES

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- Testimonials about Diphoterine® usage, available at www.prevor.com

Risk phrase codes (EC classification)

R34	Causes burns.
R35	Causes severe burns.
R36/38	Irritating to eyes and skin.

Hazard statments (CLP)

H314	Causes severe skin burns and eye damage.
H315	Causes skin irritation.
H319	Causes serious eye irritation.

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