

TOXICITY OF FIRE RESISTANT FLUIDS USED IN COAL MINES
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GENERAL

Fire resistant fluids currently used are classified in 4 categories called A, B, C, D.

Liquids A are oil water emulsions containing a maximum of 20% oil. They are made of hydrocarbons and additives and are used in hydraulic pushers and props.

Liquids B are water-oil emulsions containing a minimum of 40% water. They are not currently used in the CEE mines because none of them have been able to meet the fire resistance specifications.

Liquids C are water glycol containing additives and minimum water content is 40% ; they are used in mine car pushers.

Liquids D are synthetic based on chlorinated diphenyl and aryl-phosphates esters. Fluids composition can vary, but most of fluids we have analyzed are about of the same chemical composition when examined by infra-red spectroscopy.

As of June 1st, 1971, 274 liquids have been submitted to CEMM. Today, only 14 are being used (3A, 4C, 7D).

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These fluids can cause injuries at different levels either in normal use or during incident or accident, such as leakages, hose breaks, smelting of coupling fuses, etc...

Consequently, the E.C.C. proposed in successive reports a list of toxicological tests. The last one has been issued on March 26th, 1971.

These tests include oral toxicity or irritation value, on toxicity of aerosols at room temperature or at 150°C. and on thermal decomposition products toxicity. Each test results are marked from 0 to 10, following a precise scale. Final mark is obtained by adding up all marks multiplied by a particular ponderation coefficient for each test. If this amount is below 50, the fluid meets the specification except however if one of particular mark reaches 10.

C.E.M.M, (Centre d'Etudes Medicales Minières) equivalent : Mining Medical Study Center, has all equipment needed to carry these tests :

- Infra-red spectrography for fluids identification (A, C, D). This test is necessary to find out if no change in formulation has been introduced by the manufacturer without changing the product brand-name in adding a low quantity of a new component to modify the final result.

- Oral toxicity (A, C and D).

This test is a determination on white mice of the lethal dose by ingestion. To carry out this test, we would need about 250 mice for each fluid. For this reason, we do not run this test because it does not reproduce a normal incident. It could only happen by a voluntary ingestion, and quantity would be then defined.

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Ponderation coefficient equal 1.

Total toxicity of soluble oils and emulsions (A and D)

We carry out this test on a fish called "carassius auratus". Survival of fish in an aqueous solution of liquid at different concentration is marked. We know fish breathing and ingesting water is very sensitive to toxic products. Ponderation coefficient is 2.

Irritation value (for A, C and D).

Irritating value on skin and eyes of rabbit are determined by contact with the fluid at room temperature. Result rating is vast, but though more severe in the last report than in the previous one, it would be not severe enough for an ophtalmologist. Ponderation coefficient is higher and equal to 5.

Aerosol toxicity

We use a full-grown white rat from Wistar head. This one is kept for 3 hours in a close cabinet where spray concentration is defined. These sprays are at room temperature for fluid of "A" form, at 70°C for fluids of "C" form and at 50°C and 150°C for the "D" products. Ponderation coefficients are 4 for A and C, and 2 times 2 for D.

High temperature decomposition products toxicity

Fluids to be tested are sprayed to a heated plate using a diesel pump and injector system. Time of exposure is 3 hours like in

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the preceding test; all animals going through this test are then kept under observation for 14 days. Unfortunately observation methods are not sufficiently defined in case of sub-poisoning and practically only the death of one or several animals during the test or while observation period and ponderal curve irregularities allowed us to rate this test.

To summarize toxicological tests, in the way they are carried out today, can determine which fluids are hazardous. But some of them even if the total mark is acceptable, can create a false security. It is important to keep in mind the partial marks and sometimes to emphasize their value by a particular comment when this one is high.

In another hand, sometimes, tests result determination is difficult, and following laboratories carrying out these tests, interpretation can differ. Today only 3 labs are entitled : they are Pharmakologisches Institut Hambourg, Pâturages and CENM.

For example, when Pr. MALORNY examined a product called FYRQUEL NF (D) on rabbit eye he ascertained an erythema, leaving off after 2 days. He gave to this test a mark 2 in conformity to report N° 4 specification.

Inflammatory reaction according to coming out, rapidity, extent and duration : 1 to 5.

But inconsistent to those mentioned in report N° 2 which specified the following rating from 1 to 5 :

Conjunctive erythema and watering of eyes :

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- leaving off within 10 minutes	1
- " 1 hour.....	2
- " 6 hours	3
- " 24 hours	4
- " 5 days	5

This rating would give at least the mark 4. As the ponderation coefficient is equal to 5, we get a difference on result total of 10 ! Consequently, we have marked the eye irritation test in using this second scale. Unfortunately, some other tests are ambiguous too.

TOXICOLOGICAL TESTS CARRIED OUT ON PRESENT FLUIDS USED IN COAL MINES OF NORTH OF FRANCE.

Tested fluids :

1°) Type A : 3 fluids

- CASTROL S 4157
- LABO INDUSTRIE S 2021 C
- SHELL DROMUS B

2°) Type C : 4 fluids

- NAPHTACHIMIE NAFIC 402 H
- CASTROL HYSPIH AF/1
- NAPHTACHIMIE NAFIC H 454
- SHELL S 6694

3°) Type D : 7 fluids

- BP SHF 0200 (Pydraul A 200)
- CASTROL B 460
- PUEFINA HYDRAN FR 2
- SHELL S 7702
- SHELL S 7014
- SHELL S 7704

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We are still waiting for an other type "D", manufactured by ELF, and called E.S.T.C 724.

Equipment and test methods.

The report N°4 regarding specifications and test conditions for fire resistant fluids used in power transmission (Luxemburg, March, 26th 1971, annexe XVIII for fluids "D") define tests methods and equipment to be used. Up to now, we have carried out all the tests except oral toxicity and thermal decomposition. In order to test the 14 fluids presently used in the coal mines of the North of France, we have installed a thermal decomposition apparatus in conformity with that described in report N° 4 able to spray the fluid to be tested through a standardized injector to a hot plate kept at a fixed temperature. One cm³ of fluid is sprayed or decomposed every minute, then, cooled down to the room temperature to condensate oil vapors and decomposition gas.

Rats used in this experience breath this mixture for 3 hours and are kept under observation during the test and while a 14 days period.

A draft of this equipment is enclosed. All parameters, such as temperature, fluid flow, and air flow carrying along decomposed products are easily precisely measurable. In addition, the condensation system is particularly sophisticated. This one includes a first condenser "E", a glass flask "F" where gas temperature is cooled down to about 50°C and a condenser "G" where expanded air is injected through ejector "H". Mixture of gas coming in the cabinet are near room temperature. However, it is not possible to condensate the whole fluid vapor. Classical safety measures are taken in order to avoid laboratory pollution : the test cabinet or cage "K" is under a slight depression and the hot plate "D" is put under a ventilated hood.

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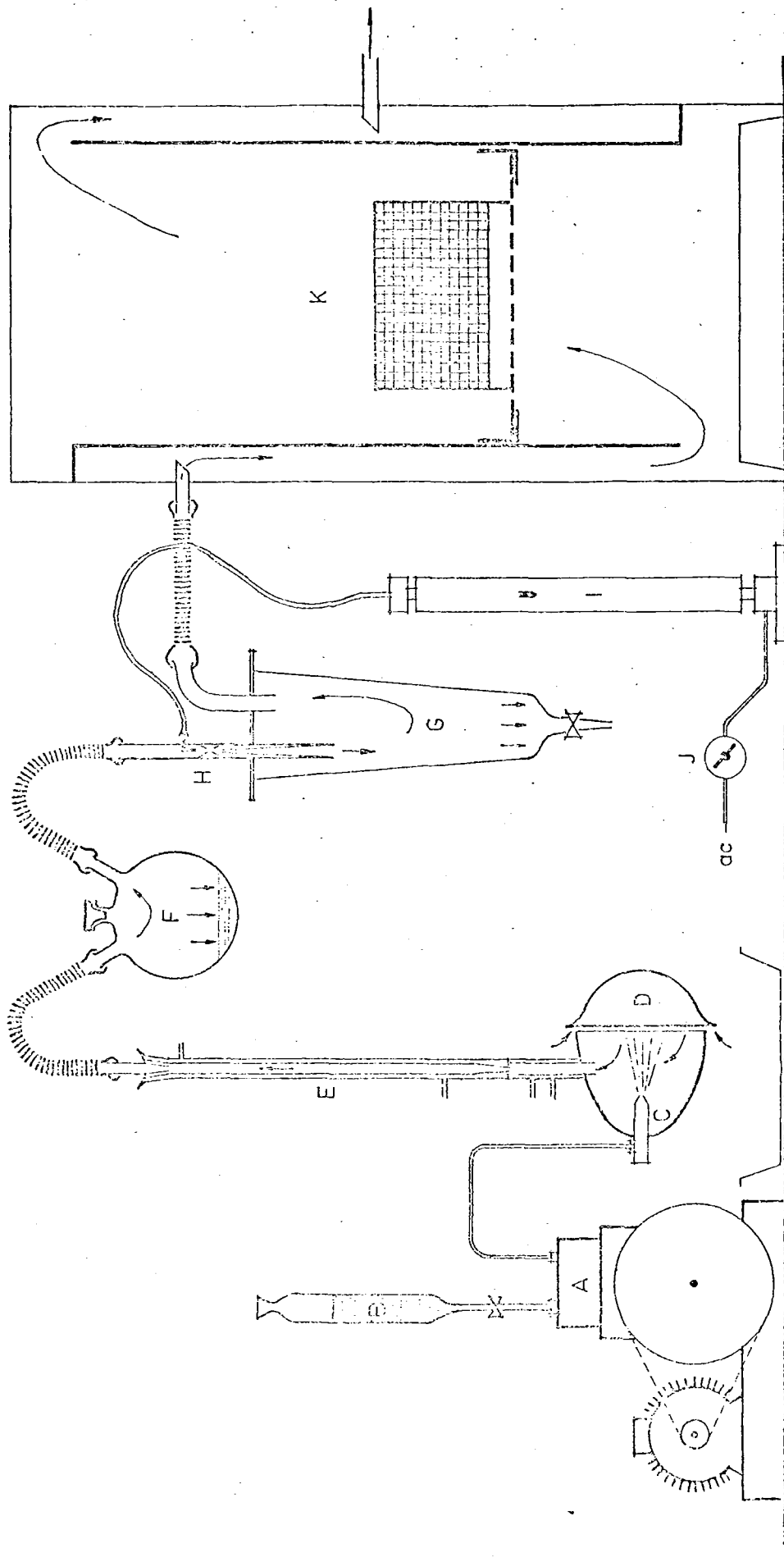
TEST RESULTS
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Results are rated following EEC recommendation (see covering letter). Particular marks assigned to each test after ponderation are listed in chart 1 with their total.

These figures obtained for each test after ponderation, for none of tested fluid, goes over 50. But result of thermal decomposition at 700°C. for all type "D", and 1 type "C", is equal to 10. According to EEC recommendation, they cannot be approved. For this reason, the thermal decomposition test set a particular problem having to be more fully examined.

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Installation pour l'essai de décomposition thermique des liquides
de transmission adéquate difficilement inflammables.



A Pompe à injection
B Liquide d'expérience
C Injecteur
D Éléments chauffants

E Condenseur
F Condenseur
G Condenseur
H Ejecteur et venturi

I Débitmètre à flotteur
J Détendeur
K Chambre d'expérience
ac Air comprimé

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Tableau 1 - Résultats d'essais de 14 liquides difficilement inflammables utilisés habituellement dans les
Mouillères du Bassin du Nord et du Pas-de-Calais.

N°	Nom du produit	Forme	Toxicité globale	Irritation		Aérosols			Décomposition thermique		Note globale
				peau	oeil	froid	70°	150°	200°	700°	
Coefficient											
1	CASTROL S 4157	A	14	0	15	3			2	3	42
2	LABO INDUSTRIEL S 2021 C	A	16	0	15	3			3	6	48
3	SHELL DRONUS B	A	14	0	15	12			3	4	48
4	BP S.H.F. 0200 (Hydraul A 200)	D		5	15		4	4	3	10	41
5	CASTROL B 460	D		5	15		4	6	7	10	47
6	PURFINA HYDRAN FR 2	D		5	15		4	6	4	10	44
7	ELF E.S.T.C. 724	D				non étudié					
8	SHELL S 7702	D		5	15		4	4	3	10	41
9	SHELL S 7014	D		5	15		4	4	4	10	42
10	SHELL S 7704	D		5	15		4	6	3	10	43
11	NAPHTACHIMIE NAFIC H 402	C	4	0	10	8			2	4	28
12	CASTROL HYSPIN AF/1	C	6	0	10	8			3	6	33
13	NAPHTACHIMIE NAFIC H 454	C	10	0	15	8			3	7	43
14	SHELL S 6694	C	4	0	10	8			3	10	35

TOXICITY OF DECOMPOSITION PRODUCTS OBTAINED DURING THE TEST
CALLED " THERMAL DECOMPOSITION"

Firstly, let us take the case of product "C", N°14, made by SHELL and called S 6694 ; it is a water glycol product with unknown additive. During the test, the animals are dead from oxycarbonyl's intoxication. The post-mortem examination did not show any macroscopic alteration and besides carbon oxide, concentration in the test cage reaches 1000 ppm, though in same conditions for the other "C" fluids N° 11, 12 and 13, this concentration was only 170, 160 and 200 ppm. To check this order of magnitude, we had to take back these 4 fluids for a second experience and find out that the N° 14 incompletely burnt when in contact with the 700° C. hot plate. Consequently, the fire resistance of this fluid must be border line.

Fluids of type D are made of polychlorinated diphenyl, sometimes blended with aromatic phosphates esters (arylphosphates). When the fluid is sprayed to the hot plate, there is a calefaction which vaporize the fluid immediately followed by a condensation giving a mist whose bigger drops are about 2.5 micron size. The turbulent medium condensation system stops the bigger drops. Animals, then, had to breath a very stable mist where the size of droplets are below 0.5 micron. The carbon oxide concentration is very low (10 ppm), and there is no phosgen (less than 0.1ppm). Consequently, it is difficult to talk about thermal decomposition or combustion. In addition, if the mist is cooled down to minus 20°C., the condensed product obtained gives exactly the same infra-red spectrum than this one obtained on nex fluid. We can conclude it is the mist coming from vaporization and condensation which poisoned animals ; we can say, consequently, it is a remake of the test called "toxicity of aerosols", but with a higher concentration (about 20g/m3).

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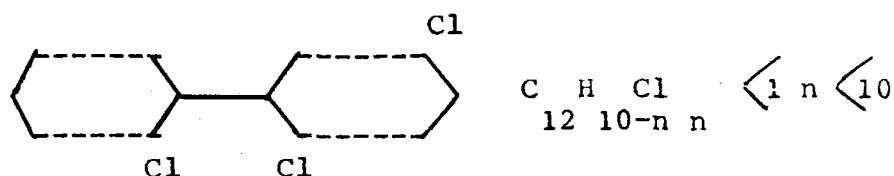
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In another hand, we have tried to decompose the fumes at high temperature by circulation through a coil heated up to 700°C. We have found in these conditions only few carbon oxide and phosgen traces. These fluids of type D are particularly stable, and their toxicity either in mist or vapor is due to their components : chlorinated diphenyl, arylphosphates, and additives.

1°) - Chlorinated diphenyl

General formula of this product is the following :



They can be mono, di, ... decachlorés. They are more or less viscous liquid at room temperature, except derivatives octo and deca wich are cristallized solids. They have a low vapor pressure and are used as plasticizers, fire proofing and high temperature lubricants. They are also able to transfer important heat quantities.

Their toxicity has to be compared to other chlorinated aromatic derivatives and particularly toxicity of chlorinated naphtalene.

The main result of PCB action is a liver attack. More the molecule of aromatic derivative contains chlorine, more the action on the liver is important. We must point out the synergic action of ethylic alcohol or carbon tetrachloride rapidly causing a liver necrosis. Consequently to exposure to a mist at 150° C for 3 hour the hepatic function showed evident problems. After few minutes PCB is accumulated in liver fats. They are acting about in the same ways that DDT, whose formula is similar.

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The post-mortem examination of animals done by the medical dept, of CEMM shows in case of death a liver volume increase and in the same time a red blackish coloration and the variegated lungs show oedema symptoms and haemorrhage appearance areas. These phenomenons are compatible with the rise of transaminases found by MALORNY demonstrating an infarctual and necrotic state of the liver.

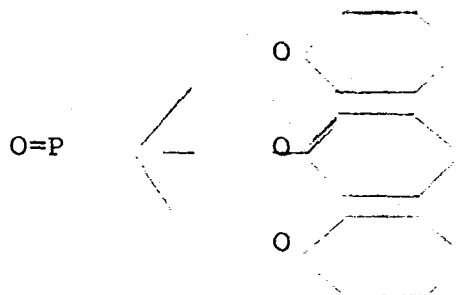
The main preoccupation is the fixation of PCB's by liver fats which is a cumulative phenomenon able to lead to severe trouble even with low amounts or brief time of exposure mainly in the case of synergic action from ethylic alcohol.

Besides it could be possible that some D fluids contain also polyphenyl ethers used in the States as high temperature lubricants and whose action on liver and kidneys is wellknown by toxicologs.

The maximum allowed dose defined by USA and USSR for PCB containing less than 50 % of chlorine is 1 mg/m3. We have already noticed a higher concentration of several grams per m3 in our test cages. This demonstrates the unrealistic character of the test called "thermal decomposition".

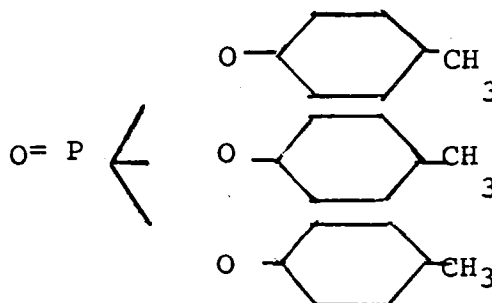
2°) Arylphosphates

The current formular is the following :



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Phenyl radicals can be substituted. For example : paratricresyl-phosphate.



used about 15 years as lubricant and hydraulic fluid in aviation. This product is probably the most hazardous of all phosphate esters. Its anticholinesterasic action can be compared to that of insecticides. In addition it provoques polyneuritis by motory degeneration and frontal callosities of spinal cord, accompanied by various haemorrhages, fatty degeneration of liver, rate, pancreas and kidneys.

3°) - ADDITIVES

We do know which products are used and of course, they can be toxic. We must point out that most of the manufacturers of fluid do not talk very much about and it is very difficult even for a specialist to analyze from an infra-red spectrum all the components of fluids type D mainly when the concentration is very low.

We must also notice that different fluid components used in type D are skin and lung tissue irritating.

The thermal decomposition test as defined by CCE subject animals to a very heavy and stable mist. Consequently, they support the toxic effect of fluid component. In the particular case of fluid this action is severe and brings animals to death.

However, it seems there is no risk that fluid used in coupling

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could be sprayed on to a hot plate ; even in case of fire, it is likely that this sort of fluid will only produce carbon oxide as phosgen is decomposed above 900° C. to give hydrochloric acid. But, if the fuse smelt between 140 and 200°C. , it could be possible to produce enough heavy mist to create hazardeous conditions, and moreover in normal conditions continuous leakage could maintain in the atmosphere a low but toxic and continuous concentration causing effect on sensibilized people and in the same time creating a chronic pathology. It is only from this sole standpoint we have to consider toxicity of type D fluids. And if we must follow EEC recommendation all these products we have tested should not be approved.

SIN-1e NOBLE, June 29th 1971

E. QUINOT

GM/dc

1.9.1971

Translated by Mr. G. MITREAU

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COVERING LETTER

TOXICITY DETERMINATION - RATING OF RESULTS

Extract from report N° 4 regarding specifications and test conditions related to fire resistant fluids used in power transmission.

Luxemburg, March, 26th, 1971.

- Global toxicity (A And C)

All the animals are alive : 0

Animals subjected to a 1.10^{-1} concentration

dead after one hour : 1

dead within one hour : 2

Animals subjected to a 1.10^{-2} concentration

dead after one hour : 3

dead within one hour : 4

Animals subjected to a 1.10^{-3} concentration

dead after one hour : 5

dead within one hour : 6

Animals subjected to a 1.10^{-4} concentration

dead after one hour : 7

dead within one hour : 8

Animals subjected to a 1.10^{-5} concentration

dead after one hour : 9

dead within one hour : 10

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Irritating value test for rabbit eye irritation

Aside from all infection :

- no reaction observed : 0
- inflammation observed according to rate
appearance, extent and duration : 1 to 5
- permanent lesion without loss of vision : 6 to 10
- loss of vision : 10

Test for rabbit skin irritation

Aside from all infection :

- no reaction observed : 0
- erythema following extent and duration : 1 to 3
- skin lesion depending from
extent and duration : 5 to 10
- death of animals tested : 10

Mist or thermal decomposition

1- No animal is dead either during the experience or
while the observation period :

- no reaction observed : 0
- irritation symptom like : perturbation
of blood circulation, nervous shock
leaving after 1 hour : 1
- " " 6 hours : 2
- " " 5 days : 3
- loss or increase of body weight

2- Some of animals are dead during the experiment or
while the observation period :

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During the experiment

	0	1	2	3
0	5	8	9	10
1	5	9	10	
2	6	10		
3	7			

Each test result is given a mark from 0 to 10, multiplied by ponderation coefficient listed herebelow :

Test	Forms	Coefficient
Oral toxicity	A, C, D	1
Global toxicity	A, C	2
Irritating value on eye	A, C, D	5
Irritating value on skin	A, C, D	5
Cold aerosol	A, C	4
Cold	D	2
Hot	D	2
Thermal decomposition		
200°	A, C, D	1
700°	A, C, D	1

A product obtaining before ponderation mark 10 in any of these tests cannot be accepted. A product, whose total marks, after ponderation reaching 50 is not accepted either.