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Document Processing Center (TS-790)
Office of Pollution Prevention and Toxic
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Attn: Section 8(e) Coordinator

Subject: TSCA Section 8(e) Submission on 1,1,5-Trihydroperfluoroamyl Acrylate

Dear Section 8(e) Coordinator:

Enclosed you will find a copy of an English translation of an Azerbaijani article entitled "TOXICOLOGIC CHARACTERISTICS OF SOME FLUOROACRYLATES" on the substance 1,1,5-Trihydroperfluoroamyl acrylate [CAS Registry No. 376-84-1]. Please note that San Esters Corporation refers to this substance as viscoat 8F. After reviewing the Agency's TSCA section 8(e) guidance, we believe that this article may be of interest to the Agency.

The researchers report limited data with respect to certain acute effects that may be deemed to represent substantial risk information. Although we have not come to any conclusions as to whether this article represents substantial risk information, it is being submitted to ensure that the Administrator is kept fully informed.

This study was published in 1983 by the M.M. Efendizade Azerbaijan Labor Hygiene and Occupational Illnesses Scientific Research Institute based on work performed by researchers

Contains No CBI

Guseinov, V. G., et al.[1] The study was obtained in Azerbaijani and subsequently translated into English. The translated study was received from the translator on Aug. 28, 1998.

Note that San Esters imports viscoat 8F and is owned in part by Mitsubishi Rayon America (MRA). As both companies, based in New York, work closely together under the requirements of TSCA, it is felt that a joint submission to EPA is appropriate. If there are any questions regarding this matter, please call Eugene Rozelman of MRA at (212) 759-5605 who is the technical contact for this submission. Mark K. Smith of San Esters is available at (212) 223-0020.

Sincerely,

Eugene Rozelman
Mitsubishi Rayon America

Mark K. Smith
San Esters

Enclosure

[1] Azerbaidzhan Medical Journal, 60:32-37 (1983).

UDK: 613.63:66:541.64:615.9

TOXICOLOGIC CHARACTERISTICS OF SOME FLUORACRYLATES

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M.M. Efendizade Azerbaijan Labor Hygiene and Occupational Illnesses Scientific Research Institute (Director: I. I. Alekberov)

The rapid growth of the scientific and technologic progress has given way to accomplishments of chemical sciences to be widely applied to various fields of agriculture. This, in return, has increased people's contact with many chemical compounds at their homes and work places. In this regard, industry toxicologists face a basic duty of preventing harmful effects from new chemical compounds, which were intended to be manufactured and applied in large amounts, and also preparing effective and long-lasting prophylactics from intoxication, in a timely manner.

Among the newly synthesized chemical compounds which belong to the complex ether group, fluoridated acrylic acid ethers, and 1.1 dihydroperfluoramilacrylates (1.1 DHPFAA), 1, 1.5 trihydroperfluoramilacrylates (1, 1.5 THPFAA) and 1, 1.7 trihydroperfluorheptilacrylates (1, 1.7 THPFHA) are considered to have greater potential for harm. The last group of above-mentioned chemicals is intended to be applied as monomers for synthesis of different polymers. Currently these compounds are being produced for experimental purposes and there are plans for the coming years to produce 100-200 tons per year of each of these chemicals for industrial use. According to the available information, up to 120 people are working in experimenting plants, trying to accomplish manufacturing and processing of these fluoracrylates. But since there is a lack of knowledge of toxic effects of these chemical compounds, they may cause negative effects on the physical well-being of those workers.

However, the other issue in relation to this one: some experimental research was done to learn more about the strong toxicity and dangers of these fluor acrylics. The results of this research is being presented to the new study.

As is clear from the physical-chemical properties (diagram no.1), the studied chemicals are from the group of chemical compounds which boil at high degrees and have a low rate of evaporation. In normal conditions they are resistant to the hydrolysis, but only in high temperatures and in alkali conditions do they respond to the hydrolysis and their polymerization begins. They are obtained by a reversible reaction of a mixture of solidified liquid solution of alkali and acrylic acid chlorohydrid with suitable fluoridate alcohol.

The literature available to us contains conflicting information about the biological effects of acrylates on an organism. It was found that when molecule masses increase in acrylate, their inhalation toxicity also increases. For methylacrylates the lethal concentration is 12.8mg/l., yet it decreases up to 1.0mg/l for heptylacrylates. In addition to that, toxicity of ether depends on the kind of acid. Ethers of methacrylic acid basically cause narcotic effects and a weak tickling sensation in the throat, yet the ethers of acrylic acid would not have a narcotic effect but would

Diagram 1

THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF FLUOACRYLATES

names and synonyms	chemical formula	aggregate condition	molecular mass	boiling point, 760mm, 20C° of the mercury column	density per gr./cm³	indicator of breakage, P2	dissolvation
1.1 dehydromerfluoramilacrylate (1.1 DHPFAA)	$C_8H_5O_2F_9$	light-coffee	304	170	1,4800	1,3289	ether, acetone, alcohol, benzol
1, 1.5 trihydroperfluoracylate (1, 1.5 THPFAA)	$C_8H_6O_2F_8$	—»—	286	170	1,440	1,3431	—»—
1, 1.7 trihydroprfluorheptilacrylate (1, 1.7 THPFHA)	$C_{10}H_6O_2F_{12}$	—»—	386	205	1,5850	1,3410	—»—

cause irritation. (G. V. Lomonov, 1978). At the same time, according to the information given by J. S. Smirnov in (1980), there is no record of narcotic effects and irritation of acrylate that carries any value.

It is known that, fluoration of the compounds greatly reduces their toxic effects (Stazek Andrej, Chtan Sbigniew et all, 1977, Laugford Nathaniel P. 1978). The study of fluorised polyethers which has a boiling point of 40 to 320⊕C, shows that, when the boiling temperature and the count of the carbon atoms in the molecule increases, toxicity decreases (H.D. Kareta, 1977).

First of all, effects of the complex ethers are characterized by the solidity of the molecule. But they get partially hydrolised in the organism and as a result of this, characteristics of their effects mostly depend on the acids created by them and partially depend on alcohol (H. V. Lazarev, 1976). The possible hydrolyzed products of the studied fluaracrylates are acryl acid and suitable fluorised alcohol.

It is known that, acrylic acid has a tickling effect in the throat and has a general toxic effect (Y. Y. Arayayeva, 1969). Highly fluorised alcohol contains poison which in turn causes irritation to the throat and they furthermore cause narcotic effects (D. J. Peterson, 1968; M. M. Airaksinen et all, 1970). It is also possible that the narcotic effects may be dominated by a tickling effect. This is seen more in alcohol which is a product of Fluor, compared to a compatible oil group alcohol.

Considering the available information, it is possible to say that the compounds which are being studied may cause tickling in the throat, narcotic and general poisonous effects on warm-blooded humans and animals.

Taking these findings into consideration, a study was conducted to determine sanitation standards of harmful substances in the air of the work place, according to the rules of methodology accepted for these types of studies (1980), the study conducted involved mice, rats, sea pigs and rabbits. Their weight varied between 18-24gr., 180-240gr., 300-400gr., 2.5-3.5kg.

Heavy toxicity, risks and the character of the toxic effects on white mice and rats were learned by naturally introducing the compounds to the stomachs of the animals. Irritation of the skin and local effects on the mucous membrane of the eyes were experimented on rabbits and sea pigs in accordance with the research methodology rules accepted in (1980) for learning of the irritating characteristics of the substances causing irritation, which heavily pollutes the air of the work place, and determining the bases of the allowed concentration limit. Resorbable effects of the

compounds on the skin were determined by applying the compound to a mouse tail and putting 2/3 of the mouse tail in a test tube filled with the compound. The results were compared with the control group in order to measure the attitude changes and sometimes mass changes and total irritation measures (YGGK) of the experimental animals. Properties of the compounds were experimented on the sea pigs by using the methods of application on the skin (O. G. Alekseyeva, L. A. Duyeva, 1978). Accumulation ability in the organism was learned through "subchronical toxicity test" (Lim R. Ket all, 1961). The results of the studies were recorded statistically by applying the Kerber and Student method to calculate the "T" measure for small groups.

When a lethal dosage of 1.1 DHPFAA, 1, 1.5 THPFAA and 1, 1.7 THPFHA was given to mice and rats, extreme poisonous effects demonstrated in a similar clinical view, the animals showed a general immobility and intoxication signs slowly developed. After a short-term awakening, it is noticed that, the animals slowly showed signs of immobility. In general, 1.5 to 2.5 hours after

Diagram 2

DANGER AND TOXICITY PARAMETERS OF 1.1 DHPFAA, 1, 1.5 THPFAA AND 1, 1.7 THPFHA WHEN GIVEN TO STOMAC IN SOLID CONDITION AND ONLY ONE TIME

name of substance	kind of animal	D1 16 per mg/kg	D1 50 per mg/kg	D1 38 per mg/kg	I D1 58	D1 D1 14	S	1 D1 58 S
1,1	mice	5600	8600±570	11400	0.11	2.03	1.41	0.082
DHPFAA	rats	800	1710±170	2750	0.58	3.4	1.87	0.31
1, 1.5	mice	2200	4400±490	7300	0.23	3.32	1.83	0.12
THPFAA	rats	430	810±62	1130	1.23	2.63	1.64	0.75
1, 1.7	mice	4980	8400±600	11200	0.12	2.3	1.52	0.08
THPFHA	rats	900	1315±86	1750	0.76	1.94	1.4	0.54

receiving the substances, they started losing coordination of their organs and their body tilted to one side. Under the influence of 1, 1.7 THPHA, it was observed that the symptoms were different to others, their whole body had a clinical-tonic irritation. Animals reacted weakly to stimuli such as sound and light. They basically died during the first 15 minutes after poisoning. During the autopsy of the dead animals, the microscopic changes in the internal organs were observed and included hyperemia and small molled anemia in the mucous membrane of the stomachs and hemorrhaged liver and spleen, and blood-filled lungs with edema.

Based on the information obtained from death of the experimental animals, some parameters of the general toxicity and hazards of the studied fluoracrylates were calculated and shown in diagram no. 2. When the studied fluoracrylates were given to stomachs, according to the severity of the toxicity and danger, they belonged to the moderate toxic group and less dangerous compounds (according to the state standards 12.1.007 -76). The sensitivity of the type of animal calculated by comparing the ratio of the moderate lethal dosage of toxicity for the most resistant kind (rats), to the moderate lethal dosage of toxicity, for the most sensitive kind (mice), the sensitivity of the kind of animals (NHE) was respectively 5; 5.4; 6.4. It is possible to say that, the fluoracrylates being studied have moderately different effects with respect to the different sensitivity of the animals.

When the compounds were injected, once or repeatedly, into the conjunctiva of the eyes of rabbits, and when it is spread on the skin, no important changes were observed by them neither on the skin nor on the mucous membrane of the eyes. The experiments made on the white mice to learn about resumption effects demonstrated no important changes of the behavior of the animals or on the physiological functions of their organs. This means, the fluoracrylates being studied, do not irritate the skin and mucous membrane of the eyes, can not be absorbed by the undamaged skin and do not have resorptive effects.

Experiments were made to learn the sensitizing characteristics of the compounds and during the applications (10 times), also during the experiments, no changes and no allergic reactions on the skin were observed. This observation, in return, brings us to conclusion that compounds do not have sensitivity creating effects.

Cumulation ability was researched on the rats with the help of "subchronic toxicity tests". The results showed that, when the compounds were given p times moderate lethal dosage was equal to 14.5gr. per kg. for 1.1 DHPFAA, 4.54 gr. per kg for 1, 1.5 THPFAA, 18.0 gr. per kg. for 1, 1.7 THPFHA. Accordingly, the cumulative samples were 1.7; 10.3 and 2.12 which indicates relatively weak cumulative ability in the organism. 1, 1.5 THPFAA does not have an effect when repeated; the organism gets used to its effect.

For the other substances studied such as organic compounds of complex ethers group which are the mix of the steam and in the air as aerosols, the approximate effective danger level (TTTS) was calculated by applying the formula shown:

$$TTTS=0.002xD15o\ (mg/kg)$$

The indicators were 3.4 mg/m^3 for 1.1 DHPFAA, 1.6 mg/m^3 for 1, 1.5 THPFAA, 2.6 mg/m^3 for 1, 1.7 THPFHA.

The substances which were studied are among the organic compounds which boil in high temperatures. Considering the possibility of the mixing of steam and high concentration of their aerosols in the actual work conditions are less, we advise for each of these fluoacrylate concentrate in the work environments approximate effective danger level of 3 mg/m^3.

Results

1. Taking the heavy toxicity and danger levels into consideration, 1.1 dihydroperfluoramilacrylate, 1, 1.5 trihydroperfluoramilacrylate and 1, 1.7 trihydroperfluorheptilacrylate are among the moderate toxic and less dangerous compounds, they have a general toxic and a weak narcotic effects. Compounds do not give an irritative effect to the skin and the mucous membrane of the eye, do not absorbed by an undamaged skin and do not have resorptive effect. They also do not cause sensitivity to the organism during application on the skin. 1.1 dehydroperfluoramilacrylate and 1, 1.7 trihydroperfluopheptilacrylate has a somewhat weak cumulative ability. On the other hand, the organism gets accustom to 1, 1.5 trihydroperfluoramilacrilate.

2. The properties which have been studied make moderate differences on the sensitivity of the different kind of animals. The most sensitive animals are the mice.

3. The approximate danger level (TTTS 3 mg/ m^3) is advised for the fluoracrylates which were studied.

[end of Azeri text]