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Alaska Airlines
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REMARKS: Final Bid Bioassay Results Arco Hoecust Safewing MPIV 1957 Green

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Very Truly yours,

By Paul Agid

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BIO RESEARCH LABORATORIES, INC.
2897 152nd Avenue N.E.
Redmond, WA 98052-5514
(206) 869-4224 FAX: (206) 869-4231

LABORATORY REPORT

ACUTE ORAL RAT TOXICITY TEST

FOR

MultiChem Analytical Services

Performed by:

BIO RESEARCH LABORATORIES, INC.

Laboratory Ref. Number: 70282
Client Sample Code: Green Safewing MP IV

Study Director _____ 5-21-97
Warren C. Ladiges, DVM Date

President & Scientific Director _____ 5/21/97
John J. Majnarich, Ph.D. Date

May 21, 1997

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I. INTRODUCTION

Bio Research Laboratories, Inc. (BRL) conducted an acute oral rat toxicity test on the sample presented by MultiChem Analytical Services on April 23, 1997. The purpose of this test was to determine the relative biological risk of potentially hazardous waste to humans and animals.

According to the "Washington State Hazzardous Waste Regulation" (WAC 173–303), hazardous waste is classified as dangerous waste or extremely hazardous waste. The Department of Ecology of Washington State uses acute oral rat toxicity tests whenever a generator has not or cannot adequately characterize the toxicity of waste. The toxicity test results determine whether a waste is classified as dangerous waste or extremely hazardous waste.

According to the established safety rules of BRL every sample is suspected to be a hazardous waste; therefore, handled with extreme care.

II. METHOD AND MATERIALS

BRL performed an acute oral rat toxicity test by following the procedures and methods explained in Biological Testing Methods DOE 80–12.

A. Apparatus:

BRL's facilities include an area for holding rats. During testing the rats were shielded from any disturbances, and the facility was well ventilated and free of fumes. There was a 12–hour light and 12–hour dark photoperiod. The rat room temperature was maintained at 23°C ± 1°C and recorded daily.

B. Test organisms:

Ten male and ten female albino rats weighing 180–227 grams were used. The rats were placed in two groups of ten. The rats were then tagged and housed inside individual stainless steel cages (7"x7"x15"). The rats were held in quarantine for seven days before starting the test. The rats were observed for signs of illness during the quarantine period in accordance with the "Animal Illness Evaluation" standard operating procedures (SOP). Rats were purchased from B&K Universal, in Kent, WA.

Food was withheld from the rats the night prior to sample material dosing; otherwise, the rats were fed and watered ad libitum.

C. **Dosing:**
"Dose" is defined as the amount of test substances administered. This is expressed as weight of the test substance in grams or milligrams per unit weight of the test animal. All rats were dosed by gavage with 5000 mg of the sample material per 1000 grams of body weight. All of the animals received the same concentration and approximate volume of the dosing solution. The volume did not exceed 5 mL per rat.

D. **Test Duration:**
The test began on May 6, 1997 and ended on May 20, 1997. The rats were observed for 14 days for mortality and clinical pharmacological or toxicological signs.

E. **Sample Test Substance:**
An evaluation of the integrity of the test samples was made upon receipt as to packaging deficiency, proper weight of sample for testing, possible mishandling during shipping, or any other visible defects. Any deficiencies were noted and used in the final interpretation of the data.

Date of Delivery: April 23, 1997
Physical & Chemical Characteristics: Green viscous liquid
Client Reference Code: Green Safewing MP IV
Vehicle: Water was used as a suitable vehicle. The test substance was then administered in a single dose by gavage.

F. **Observation of Animals:**
Observations were made for any toxicity effect immediately after dosing at one and four hours and daily thereafter for a period of 14 days. From cageside the rats were carefully observed daily for the following:

1. The skin and fur.
2. Eyes and mucous membranes.
3. Respiratory system.
4. Circulatory system.
5. Autonomic and central nervous system.
6. Somatomotor activity and behavior pattern.
7. Tumor, convulsions, salivation, diarrhea, lethargy, and coma.

The individual weight of the animals was determined immediately before the test substance was administered, weekly, and at death. At termination of the test all of the surviving rats were weighed and sacrificed.

G. **Gross Necropsy:**

Gross necropsy was performed on rats that died during the test, and on the rats that were sacrificed at termination. The gross necropsy included examinations of:

1. The external surface of the body.
2. The thoracic and abdominal cavities and their contents.

III. RESULTS

A. **Body Weight:**

The mean weekly body weight for the rats dosed 0 mg/kg (control), and 5000 mg/kg are shown in the following table:

Table I: *Mean Weekly Body Weight*

Sample/Dosage	Mean Body Wt. (grams)			
	day 0 (5/6/97)	day 7 (5/14/97)	day 14 (5/20/97)	14 Day Wt. Gain (g/rat)
Control, male (5) 0 mg/kg	218.6	302.0	335	116.4
Control, female (5) 0 mg/kg	200.2	245.0	258.6	58.4
Sample #760282, male (5) 5000 mg/kg	221.6	302.0	328.6	107.0
Sample #760282, female (5) 5000 mg/kg	191.2	236.8	244.4	53.2

Number in parentheses ( ) is the number of animals results are based on.

III. RESULTS (Cont.)

B. **Cageside Observation:**

All of the rats appeared healthy and ate normally.

C. Mortality:

There were no mortalities.

D. Gross Necropsy:

All the animals appeared normal and healthy. There were no signs of typical toxicity effects. All the organs examined on necropsy appeared normal. Specifically the organs examined macroscopically were the liver, spleen, kidneys, adrenals, bladder, ovaries (females), testes (males), heart, lungs, and thymus gland.

Table 2: Raw Data Sheet

DATA SHEET FOR ACUTE ORAL RAT FEEDING TEST

INDUSTRY Multi Chem Analytical Svs. BIO RESEARCH LABORATORIES Sample # Controls

TOXICANT DI Water ANALYST J.J.M., W.L.

COLLECTOR BRL BEGINNING TIME /DATE 9:30 am, 5/6/97

DATE SAMPLE COLLECTED 5/6/97 ENDING TIME /DATE 9:40 am, 5/20/97

TEST ORGANISM Sprague Dawley Rats DOSAGE LEVEL 5000 mg/kg

RAT #	Weight			Dose	OBSERVATIONS AND DATES															COMMENTS
	0	7	14		4hr	5/7	5/8	5/9	5/10	5/11	5/12	5/13	5/14	5/15	5/16	5/17	5/18	5/19	5/20	Necropsy
705 M	213g	295g	320g	2.1ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	Normal Organs
706 M	228g	310g	345g	2.3ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
707 M	226g	320g	342g	2.3ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
708 M	210g	280g	301g	2.1ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
709 M	216g	305g	351g	2.2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
710 Fe	205g	246g	258g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
711 Fe	195g	236g	249g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
712 Fe	200g	241g	251g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
713 Fe	203g	257g	275g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
714 Fe	196g	245g	260g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
Initials	J.M./K.	J.M./K.	J.M./K.	J.J.M.	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	"

Table 3: Raw Data Sheet

DATA SHEET FOR ACUTE ORAL RAT FEEDING TEST

INDUSTRY Multi Chem Analytical Svs. BIO RESEARCH LABORATORIES Sample # 70282

TOXICANT Green Safewing MP IV ANALYST J.J.M., W.L.

COLLECTOR Brian Sender BEGINNING TIME/DATE 9:15 am, 5/6/97

DATE SAMPLE COLLECTED 4/22/97 ENDING TIME/DATE 9:30 am, 5/20/97

TEST ORGANISM Sprague-Dawley Rats DOSAGE LEVEL 5000 mg/kg

RAT #	Weight			Dose	OBSERVATIONS AND DATES															COMMENTS
	0	7	14		4hr	5/7	5/8	5/9	5/10	5/11	5/12	5/13	5/14	5/15	5/16	5/17	5/18	5/19	5/20	Necropsy
695 M	213g	305g	340g	2.1ml	✓	✓	✓	✓	✓	✓	✓	✓	—	✓	✓	✓	✓	✓	✓	Normal Organs
696 M	218g	295g	326g	2.2ml	✓	✓	✓	✓	—	✓	✓	✓	✓	✓	—	✓	✓	✓	✓	"
697 M	229g	313g	343g	2.3ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
698 M	230g	310g	314g	2.3ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	—	✓	—	✓	✓	✓	"
699 M	216g	287g	318g	2.2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
700 Fe	195g	240g	240g	2ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
701 Fe	183g	239g	252g	1.9ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
702 Fe	186g	233g	240g	1.9ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
703 Fe	194g	235g	236g	1.9ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
704 Fe	193g	235g	254g	1.9ml	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	"
Initials	J.M./S.	J.M./S.	J.M./S.	J.J.M.	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	SC	J.J.M.

ORALRAT.XLS

IV. DISCUSSION AND CONCLUSIONS

The purpose of this acute oral toxicity test was to provide information on rat health hazards likely to arise from a single oral exposure. Data from an acute study serves as a basis for classification, labeling, and packaging. Also, data is evaluated to determine whether the median lethal dose (LD_{50}) was below or above the administered dose.

"LD_{50} oral (median lethal dose)" is a statistically derived single dose of a substance that can be expected to cause death in 50 percent of the animals when administered by the oral route. The LD_{50} value is expressed in terms of weight of the test substance (g, mg) per unit weight of the test animal (e.g., mg/kg).

According to the Washington State Hazardous Waste Regulation (WAC 173–303) and Washington State Department of Ecology (DOE) "Acute Oral Rat Toxicity Test" (DOE 80–12, revised June 1991), a waste substance can be classified as an extremely hazardous waste (i.e., $LD_{50} \leq 100$ mg/kg) or a dangerous waste (i.e., $LD_{50} \leq 5000$ mg/kg). The death of two or less test animals per dose will be statistical evidence that the LD_{50} is greater than the standard at the 95 percent confidence level.

BRL Sample #70282; Green Safewing MP IV

In conclusion, with no mortalities associated with toxicity at the 5000 mg/kg doses, this sample is not considered to be a dangerous waste. The average weight gain over the two week period was 116.4g for the control males versus 107g for the test males per rat. The average control male gained 11.4g more than the test male. The control females gained a total of 58.4g versus the test females which gained a total of 53.2g per rat over the same two week period. The average control female gained 5.2g more than the test female. The total weight gains were comparable in both the test and the control groups.

V. PROFESSIONAL STAFF

John J. Majnarich, Ph.D., President & Scientific Director

F. Sadri, Ph.D., Director of Research

Warren C. Ladiges, DVM; Director of Veterinary Services

Wanda R. Seaman, M.S., Microbiologist

Chris V. Rathe, Vice President of Marketing

BIO RESEARCH LABORATORIES, INC.
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LABORATORY REPORT

HAZARDOUS WASTE CHARACTERIZATION

FOR

MultiChem Analytical Services

Performed by:

BIO RESEARCH LABORATORIES, INC.

2897 152nd Avenue NE
Redmond, WA 98052

BRL #	Client Code
70281	Green Safewing MP IV

May 3, 1997

Study Director Sylvia R. Cooper 5/3/97
Sylvia R. Cooper Date

President & Scientific Director John J. Majnarich 5/3/97
John J. Majnarich, Ph.D. Date

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STATIC ACUTE FISH TOXICITY TEST

I. INTRODUCTION

Bio Research Laboratories, Inc. (BRL) carefully performed a Hazardous Waste Characterization of the test sample material presented by **MultiChem Analytical Services** in accordance with the requirements of the Washington State Hazardous Waste Regulation (WAC 173–303). BRL followed the procedure issued by the Washington State Department of Ecology "Biological Testing Methods: Part A. Static Acute Fish Toxicity Test" (DOE 80–12, revised August, 1996). This test method is strictly a range–finding test and does not define the actual median lethal concentration (LC_{50}). The LC_{50} is defined as "the concentration of substance that kills fifty percent of the organisms being tested within 96 hours".

II. SOURCE AND CONDITIONS OF ORGANISMS

Rainbow Trout (*Oncorhynchus mykiss*) were used as test organisms. The fish were obtained from Nisqually Trout Farm. Ten fish were selected at random. The average weight and standard length of each of the selected fish was measured. The standard length is defined as the distance between the tip of the snout to the end of the caudal peduncle. These particular fish had an average weight of 0.84 g, which gives the ratio of flesh to water of 0.44 g/L. The length ranged from 35 to 54 mm, which gives a long to short ratio of 1:1.

When the fish were brought into BRL's facility, they were quarantined for a minimum of seven days, and appeared to be disease free. During this period, the fish were held at a stable temperature (16°C ± 2°C). There was constant water quality in an aerated flow–through system with a flow rate of approximately 30 liters per hour. During the holding period the fish were observed daily for signs of disease, stress, injury, hemorrhaging, and external parasite.

III. FACILITY AND EQUIPMENT

A. Holding Facilities

BRL's facilities include an area for holding and acclimating fish while providing a constant temperature of 15°–16°C using carbon filtered tap water. The air used for aeration is free of oil and fumes. The test organisms were shielded from any disturbances. The facility is well ventilated and free of fumes. There is a 16–hour light and 8–hour dark photoperiod. Special care is taken to guard against contamination of the fish holding tanks.

B. Holding Chambers

The test chambers are located in a special room with the temperature remaining constant at 12°C ± 1°C. These test chambers are made from glass (11"x21"x10"), which exceeds the DOE required dimensions. Before using, test chambers are cleaned thoroughly. A standard cleaning procedure is followed: Detergent or acetone is used to remove organic compounds; 5% concentration of nitric acid is used to remove metals and bases; and 200 mg hypochlorite/L is used for disinfection. Finally, the test chambers are rinsed with dilution water before the start of the test.

C. Dilution Water

The dilution water used in this investigation was filtered through a one micron pre–filter, two large carbon beds and a one micron post–filter. A fresh sample of dilution water was routinely tested for residual chlorine. Hardness, alkalinity, and specific conductance were also routinely tested by certified EPA methodology. The dilution water in the test chambers was intensively aerated by air stones prior to introducing the sample test material.

1. <u>Adjusting Dilution Water Hardness</u>
   The hardness and alkalinity of the dilution water were adjusted to 80–100 mg/L as $CaCO_3$ and 60–70 mg/L as $CaCO_3$, respectively, by adding the following solutions:

   1. 6 mL of KCl stock solution (8 g/L) per tank.
   2. 7 mL of $MgSO_4$ Anhydrous stock solution (120 g/L) per tank.
   3. 14 mL of $NaHCO_3$ stock solution (96 g/L) per tank.
   4. 280–300 mL of $CaSO_4 \cdot 2H_2O$ stock solution (10 g/G) per tank.

IV. SAMPLE TEST MATERIAL

An evaluation of the integrity of the test sample was made upon receipt to detect packaging deficiency, proper volume of sample for testing, and possible mishandling during shipping or any other visible defects. Any deficiencies were noted and used in the final interpretation of data.

Date of Collection: April 22, 1997
Date of Delivery: April 23, 1997
Accepted by: Sylvia R. Cooper
Physical & Chemical characteristics of sample: Green viscous liquid

V. TEST PROCEDURE

The fish were not fed during and 48 hours prior to testing. All test chambers were inspected for basic water chemistry, temperature, and mortality at time 0, 4, 18, and 24 hour periods and every 24 hours thereafter. It was extremely important that procedures outlined were used to determine whether test organisms were dead, immobilized, or otherwise affected.

A. Control Group

Thirty (30) representative fish were placed in three replicate test chambers with 10 fish per chamber. These chambers were used as control and they were free of the sample test material.

B. Treated Group

The sample test material was added to the dilution water in the test chambers at 100 mg/L. Thirty (30) representative fish were placed in three replicate test chambers with 10 fish per chamber for each exposure level within 30 minutes after the test sample was added to the dilution water.

VI. TEST METHODS AND CONDITIONS

Table I. Static Acute *Oncorhynchus mykiss* (Rainbow trout) toxicity test.

Client: MultiChem Analytical Services

Lab. Ref. No. 70281
Date: 04/28/97 – 05/02/97

Test Protocol:	Biological Testing Methods: Part A. Static Acute Fish Toxicity Test. DOE 80–12 & WAC 173–303–110(3).
Test Material:	Green Safewing MP IV
Test Organism:	*Oncorhynchus mykiss* (Rainbow trout)
Number/Container:	Ten
Volume/Container:	19 L
Test Concentrations:	100 mg/L and 0% control
Replicates:	Three
Reference Toxicant:	Sodium Chloride (NaCl)
Test Duration:	96 hours
Control Dilution:	Moderately hard synthetic freshwater
Test Chambers:	10–gallon glass aquariums
Lighting:	Fluorescent bulbs (50–100 foot candles)
Photoperiod:	16 hours light; 8 hours dark
Temperature:	12°C ± 1°C
Chemical Data:	Dissolved oxygen, and pH are measured at initiation and every 24 hours; Specific conductivity are measured at test initiation and termination; Hardness and alkalinity is measured at test initiation
Effect Measured:	Mortality
Test Acceptability:	Control mortality less than 10%

Bio Research Laboratories, Inc. *May 3, 1997*

Table II. Static Acute Trout Toxicity Test Data Sheet

Sample	Green Safewing MP IV	Test Dates	04/28/97-05/02/97	Page	1 of 1
Source	MultiChem Analytical Services	Test Organisms	Rainbow Trout	Start Time	2 PM
Lab. Ref. No.	70281	Dilution Media	Mod.hard synth.water	End Time	2 PM
Temperature	12°C ± 1°C	Volume/Container	19L/10G tank	Staff	JJM, SC

Group	Conc mg/L	No. of Org.	Immobile/Mortality 0	24	48	72	96	Total Mort	Dissolved Oxygen (mg/L) 0	24	48	72	96	pH 0	24	48	72	96	Conductivity (µS) 0	96
Control	0 a	10	0	0	0	0	0	0	11.4	10.3	9.8	9.4	9.2	7.4	7.3	7.3	7.2	7.1	220	250
Control	0 b	10	0	0	0	0	0	0	11.4	10.5	10.1	9.7	9.4	7.4	7.3	7.2	7.1	7.1	220	240
Control	0 c	10	0	0	0	0	0	0	11.5	10.5	10.3	10.0	9.6	7.5	7.4	7.4	7.3	7.2	220	250
70281	100 a	10	0	0	0	0	0	0	11.7	10.2	9.8	9.2	8.8	7.4	7.4	7.4	7.3	7.3	220	250
70281	100 b	10	0	0	0	0	0	0	11.6	10.3	10.0	9.8	9.4	7.5	7.4	7.4	7.3	7.3	220	240
70281	100 c	10	0	0	0	0	0	0	11.6	10.3	10.0	10.0	9.4	7.4	7.4	7.4	7.3	7.3	230	240

	Control	100 mg/L
Total Hardness (mg/L as $CaCO_3$)	67	63
Total Alkalinity (mg/L as $CaCO_3$)	60	59

Sample Description Green viscous liquid
Average Weight 0.84 g Mean Length 43.8 mm Longest 54 mm Shortest 35 mm
Ratio (long/short) 1:1 Number of organisms per chamber 10 Ratio of flesh to water 0.44 g/L
Comments

VII. RESULTS

A. Testing of Sample Material 70281 (Green Safewing MP IV) at 100 mg/L

The chemical and physical data of treated (100 mg/L) and control test chambers are shown in Table II. There was 0 % mortality or 0 out of 30 mortalities at 100 mg/L group and no deaths for the control group. The sample material at 100 mg/L had no significant effects on the pH, total hardness, total alkalinity, and conductivity of dilution water (Table II).

III. DISCUSSION AND CONCLUSIONS

The results of this study clearly indicate that the sample material had only a slight effect on the conductivity, pH, total hardness, and total alkalinity of the dilution water as the concentration of the material were increased to 100 mg/L (Table II).

The sample material did not effect oxygen saturation of the dilution water when the concentration was increased to 100 mg/L (Table II). There was nothing unusual noted about the test conducted. There were no deficiencies noted upon receipt of the sample.

According to Washington State Hazardous Waste Regulation (WAC 173-303-110(3)), to determine if a waste is Dangerous Waste (DW), a person must first establish the toxicity range of a waste by means of the 100 mg/L acute static fish test or the 5000 mg/kg oral rat test. To determine if a waste is Extremely Hazardous Waste (EHW), a person must establish the toxicity range of a waste by means of the fish bioassay at 10 mg/L or the rat bioassay at 50 mg/kg.

For a waste material to be designated a dangerous waste (DW), greater than ten cumulative deaths out of 30 test organisms must occur within 96 hours at a concentration of 100 mg/ L. This waste is said to have an LC_{50} less than 100 mg/L at 95 percent confidence level.

In conclusion:

> **Sample #70281 (Green Safewing MP IV) – with zero mortalities at 100 mg/L concentration, the tested sample is said to have an LC_{50} of greater than 100 mg/L and is not considered to be a dangerous waste.**

PROFESSIONAL STAFF

John J Majnarich, Ph.D., President & Scientific Director

F. Sadri, M.S., Ph.D., Director of Research

Warren C. Ladiges, DVM; Director of Veterinary Services

Wanda R. Seaman, M.S., Microbiologist

Chris V. Rathe, Vice President and General Manager

[redacted]

Static Acute Trout Toxicity Test Data Sheet

Sample: Green Safewing MP III
Source: Multichem Analytical 3rd
Lab. Ref. No.: 70281
Temperature: 12°C ± 1°C

Test Dates: 4/28/97 - 5/2/97
Test Organisms: Rainbow Trout
Dilution Media: Mod. Hard Synth. Water
Volume/Container: 1 gal/10 gal

Page: 1 of 1
Start Time: 2pm
End Time: 2pm
Staff: JM, JC

Group	Conc mg/L	Rep	# of Org.	Invertebrate/Mortality 0	24	48	72	96	Total Mort	Dissolved Oxygen (mg/L) 0	24	48	72	96	pH 0	24	48	72	96	Tot. Hardness (mg/L as $CaCO_3$) 0	96	Tot Alkalinity (mg/L as $CaCO_3$) 0	96	Conductivity (µS) 0	96
Control	0	A	10	0	0	0	0	0	0	11.4	10.3	9.8	9.4	9.2	7.4	7.3	7.3	7.2	7.1	80	90	60	60	220	251
Control	0	B	10	0	0	0	0	0	0	11.4	10.5	10.1	9.7	9.4	7.4	7.3	7.2	7.1	7.1	60	70	60	60	220	241
Control	0	C	10	0	0	0	0	0	0	11.5	10.5	10.3	10.0	9.6	7.5	7.4	7.4	7.3	7.2	60	60	60	62	220	252
70281	100	A	10	0	0	0	0	0	0	11.7	10.2	9.8	9.2	8.8	7.4	7.4	7.4	7.3	7.3	60	60	60	64	220	252
70281	100	B	10	0	0	0	0	0	0	11.6	10.3	10.0	9.8	9.4	7.5	7.4	7.4	7.3	7.3	60	60	56	60	220	246
70281	100	C	10	0	0	0	0	0	0	11.6	10.3	10.0	10.0	9.4	7.4	7.4	7.4	7.3	7.3	70	60	60	60	230	246

Sample Description: Green viscuous liquid Average Weight: 0.84g Mean Length: 43.8mm Longest: 54 mm Shortest: 25mm Ratio (long/short): 1:1
Number of organisms per chamber: 10 Ratio of fish to water: 0.44g/L Comments:

MEMBER

ARCO Chemical Company
3801 West Chester Pike
Newtown Square, PA 19073
Telephone 610 359 2284
Fax 610 359 7207

Andrew B. Lewis
Senior Sales Representative
Aircraft Deicers

March 27, 1997

Alaska Airlines
PO Box 68900
Seattle, WA 98168-0900

Attention : Peggy McCluskey

Dear Peggy;

The following is the environmental information per 3.1.1 of SAE AMS 1428A for Hoechst Safewing MP IV 1957 Green. The information contained herein is as was presented to ARCO Chemical Company by the manufacturer of the material, Hoechst AG.

BOD_5	370mg/g
COD	830mg/g
Biodegradability after 3 days	>95%
Aquatic Toxicity LC_{50} (Fathead Minnow)	~1400mg/l

If you have any other questions or requirements please call me at (610) 359-2284.

Yours truly,
ARCO Chemical Company

A.B.Lewis, P.Eng.

P.2/18

AR 024815

IN THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF COLUMBIA

NATURAL RESOURCES DEFENSE COUNCIL, INC.; PUBLIC CITIZEN, INC.,

Plaintiffs,

v.

CAROL M. BROWNER, ADMINISTRATOR, U.S. ENVIRONMENTAL PROTECTION AGENCY,

Defendant,

and

AMERICAN FOREST & PAPER ASSOCIATION; et al.,

Intervenor-Defendants.

Civil No. 89-2980 (RCL)

DEFENDANT'S UNOPPOSED MOTION TO MODIFY CONSENT DECREE

On October 30, 1989, Natural Resources Defense Council, Inc. ("NRDC") and Public Citizen, Inc. (collectively "Plaintiffs") brought this action against the United States Environmental Protection Agency ("EPA"), alleging that EPA had failed to issue a plan for establishing effluent guidelines for various industry categories, as required by section 304(m) of the Clean Water Act ("CWA"), 33 U.S.C. § 1314(m). Under the terms of the Consent Decree entered on January 31, 1992 in this case, EPA was required to propose and take final regulatory action with respect to effluent guidelines for eleven specified industry categories; to complete eleven studies aimed at selecting additional guidelines; to start, propose and take final action on eight other unspecified industry categories; and to publish effluent

guidelines plans in the Federal Register. To date, EPA has completed four rulemakings and seven studies, and has proposed four additional rules.

Since 1992, EPA has requested, and this Court has granted, several unopposed extensions of deadlines in the Decree.[1] However, in early 1996, EPA concluded that the timeframes set forth in the Decree are based on rulemaking schedules and budget estimates that have turned out to be somewhat unrealistic. For example, due to EPA's budgetary and staffing limitations and changes to the regulatory process (e.g., amendments to the Paperwork Reduction Act), the time EPA currently needs to complete a guideline has grown from five years -- as contemplated by the original Decree -- to seven years. As a result, EPA initiated negotiations with NRDC, on behalf of Plaintiffs, for a

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mid-course re-examination of the obligations in the Decree. Those negotiations have resulted in the following proposed modifications to the Decree, which Plaintiffs and Intervenors American Forest & Paper Association, Chemical Manufacturers Association and National Association of Metal Finishers do not oppose.

Proposed Modifications To The Decree

By this motion, EPA respectfully requests this Court to modify the Consent Decree entered in this case as follows:

A. Add new WHEREAS clause to page 3 of Decree prior to penultimate WHEREAS clause, to read as follows:

> WHEREAS, EPA and plaintiffs have agreed to additional provisions contained in a Settlement Agreement, dated January 31, 1997;[2]

[2] Concurrent with the filing of this motion, EPA and NRDC, on Plaintiffs' behalf, have executed a Settlement Agreement that, inter alia, details the Agency's current intent to propose a joint Clean Air Act/Clean Water Act rule for the Pharmaceutical Manufacturing category by April, 1998, and describes the contents of three upcoming studies referenced in paragraph 3 of the Decree. Because the instant case was brought under the CWA, it was necessary to memorialize EPA's intentions under the CAA outside of the Decree. Prior to the filing of this motion, Plaintiffs and Intervenors were provided copies of the Settlement Agreement, which is attached for informational purposes at Exhibit A.

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8. Chemical Formulators and Packagers	1995	April, 1997 [was Jan. 31, 1997]
9. Paperboard	1997 [was 1996]	1998 [was 1997]
10. Urban stormwater	1997 [was 1996]	1998 [was 1997]
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CONCLUSION

For the reasons set forth above, EPA respectfully requests this Court to grant the Agency's unopposed motion to modify the Consent Decree.

Respectfully submitted,

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DATED: January 31, 1997

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DATED: January 31, 1997

WORKING CO

Bioremediation of Ethylene Glycol

The nation wide estimate for use of deicing products in aircraft deicing situations is 11.5 million gallons/yr (D'Itri 1992). The active and predominant components of these deicing products are ethylene glycol and propylene glycol. The environmental effects from ethylene and propylene glycol contamination in storm water runoff from airport deicing activities are a major concern of the "Clean Water Act" regulators. Non point source runoff of glycols from deicing activities needs to be controlled. One feasible alternative is retention and bioremediation before release to the receiving waters.

Although ethylene and propylene glycol are not acutely toxic in the concentrations that are typically found in runoff or receiving waters they are highly, rapidly, biodegradable. The biodegradation is so rapid that it depletes the dissolved oxygen levels and thus threatens aquatic life. It has been determined that at 20°C ethylene glycol degrades within 4 days. At 4°C degradation is markedly slower however almost 100% degradation occurs by the 14th day (Evans and David, 1974). Eutrophication and malodorous vapors result from the degradation and cause environmental concern. Biodegradation studies of ethylene glycol have been conducted (however it appears none have been done recently) using river water samples and various control temperatures. However, no particular species has been isolated. I believe this is because a wide variety of microorganism are capable of glycol degradation.

Ethylene glycol oxidation can occur both aerobically and anaerobically, however aerobic degradation appears to occur much more rapidly (O_2, being the electron acceptor of choice). Anaerobic degradation occurs in at least one situation where SO_4 or SO_3 serve as the electron acceptor resulting H_2S formation.

Aerobic oxidation of Ethylene Glycol $(CH_2OH)_2$

$(CH_2OH)_2$ serves as the electron donor according to the following reaction

$$(CH_2OH)_2 + 2H_2O \Rightarrow 2CO_2 + 10H^+ + 10e^-$$

With O_2 as the electron acceptor the overall energy reaction would be written as below

$$(CH_2OH)_2 + 2\frac{1}{2}O_2 \Rightarrow 2CO_2 + 2\frac{1}{2}H_2O$$

The oxidation demand for $(CH_2OH)_2$ can be calculated as follows

$$\frac{2.5 mole O_2}{1 mole (CH_2OH)_2} \times \frac{32 g O_2}{1 mole O_2} \times \frac{1 mole (CH_2OH)_2}{62 g (CH_2OH)_2} = 1.28 g\ OD/g\ (CH_2OH)_2$$

The above calculation provides the chemical oxidation demand of ethylene glycol. The biochemical demand is considered to be 0.4 to 0.7g/g (Transport Canada, 1985; FAA 1990) Applications of ethylene glycol can very from 10 gallons per application to 1,000 gallons per application with average daily uses being near 3,000 gallons throughout the deicing season. Converting this average to grams yields a rough daily average of 1.47×10^6 grams of ethylene glycol discharging in the storm water runoff. Due to the rapidity of degradation the BOD and COD levels in the receiving waters will shoot up to 8.82×10^5 and 1.88×10^6 respectively as the runoff enters and bacterial degradation starts.

One particularly interesting thing from a paper written by Evans and David in, 1974 showed that degradation occurred more rapidity in the samples (batch type set-up) containing some of the river sediment. The samples that were strictly river water (low TSS, fewer bacteria) had degradation curves with a lag period at the beginning progressing to a more rapid degradation after the first few days. Whereas the samples containing sediment (a higher TSS - thus more bacteria) produced a zero order curve with no lag or change in the degradation rate. (see graph below). A higher initial concentration of bacteria in the system resulted in a more rapid degradation of the substrate (glycol) and a zero order curve that was only dependent on the rate constant not substrate concentration.

Biodegradation of ethylene glycol occurs readily. Ethylene glycol must be an excellent (high energy yielding) electron donor to be used by the microorganisms so rapidly. This factor in itself causes most of the ethylene glycol environmental concerns in the form of depleted dissolved oxygen for the rest of aquatic life. Fish kills have been reported as a result of deicing runoff into receiving waters. Over growth of the bacteria degrading the ethylene glycol and the fumes (H_2S) released during anaerobic degradation are also concerns resulting from contamination from airport deicing runoff.

Water Research Vol. 8, pp. 97 to 100. Pergamon Press 1974. Printed in Great Britain.

BIODEGRADATION OF MONO-, DI- AND TRIETHYLENE GLYCOLS IN RIVER WATERS UNDER CONTROLLED LABORATORY CONDITIONS

W. H. Evans and E. J. David
Laboratory of the Government Chemist, Cornwall House, London, SE1 9NQ, England

(*Received* 14 *June* 1973)

Abstract—The biodegradation of mono-, di- and triethylene glycols has been evaluated in river waters under controlled laboratory conditions. A recently developed method for the direct monitoring of these glycols at low concentrations indicates that they degrade according to the bacterial state and temperature of the river water. Monoethylene glycol degrades completely at 20°C within 3 days; at normal winter river temperatures not exceeding 8°C, monoethylene glycol is degraded partially or completely within 7 days depending on the river. Di- and triethylene glycols will be removed partially or completely within 7 days at 20°C, but for winter conditions of river flow and temperature, degradation will be minimal within this period.

INTRODUCTION

Deicing agents, containing glycols often mixed with a volatile alcohol such as isopropanol, are being increasingly used for removal of frost and ice from aircraft and airfield runways. Airfield drainage may subsequently contaminate surface waters, abstracted for potable purposes or ingested by field or domestic animals, with undesirable levels of these glycols. Additionally, these glycols may be harmful to aquatic life. The biochemical oxygen demand of the glycols may reduce the dissolved oxygen concentration of natural waters. The latter, however, is not considered serious at the levels likely to be encountered in surface waters. Oral ingestion of both mono- and diethylene glycol has a toxic action on the kidneys and central nervous system, but lethal doses to domestic animals are high with an LD_{50} in the order of 10 ml kg^{-1}; triethylene glycol is considered to be non-toxic and a mild bacteriocide (Browning, 1965). The chronic toxicity of mono- and diethylene glycols to small mammals has been investigated. The most recent evidence (Plugin, 1968) suggests that a dose of 0·05 mg kg^{-1} (equivalent to 1 mg l^{-1} of ingested water) had no long term effects and it was recommended that the maximum permissible concentration of these glycols in water supplies should be 1 mg l^{-1}.

The biodegradation of these glycols has not been monitored in the past because of the absence of suitable methods for their determination. An indirect measure of their degradation by assessment of the Biochemical Oxygen Demand (BOD) has been reported (Hatfield, 1957). This estimation employed acclimatized bacteria in settled domestic sewage with levels of 300–500 mg l^{-1} of each glycol. While the monethylene glycol gave an immediate oxygen demand the other glycols gave none, possibly because of the toxic effects on microorganisms of the high levels of each glycol employed. Aircraft run-offs would be considerably diluted in surface water and assessment of the biodegradation in the range 1–10 mg l^{-1} would be desirable. A direct method for the monitoring of these glycols at low concentrations in river waters has been recently developed (Evans and Dennis, 1973), and this provides a suitable means for assessment of the biodegradation of these glycols in river waters for a range of temperature.

EXPERIMENTAL

Method of analysis

The method employed for monitoring glycol levels (Evans and Dennis, 1973) is based on the oxidation of the glycols with acidified permanganate to the corresponding aldehydes and reaction of these aldehydes with 3-methylbenzothiazolone hydrazone hydrochloride to give green cationic chromogens measured at 630 nm. This method gives a linear response for the range 0–6 mg l^{-1} of each glycol, employing 5-ml standard solutions. Typical optical density response for each glycol, in 10 ml of final solution, is: monoethylene glycol 0·130 mg^{-1} l^{-1}; diethylene glycol 0·053 mg^{-1} l^{-1}; triethylene glycol 0·059 mg^{-1} l^{-1}. Recovery of each glycol added to river waters, in the range 1–5 mg l^{-1}, averaged 100·5 per cent with a precision of 7 per cent. River sample blank readings, to compensate for natural

interferences, were monitored concurrently enabling added concentrations of glycols to be determined at levels above 0·2 mg l^{-1}.

Biodegradation experiments

Freshly-collected river waters, designated A, B, C and D, of varying composition from different topographic origins were employed for the biodegradation of the three glycols. River A was a major watercourse with a relatively constant slow flow rate and a constant river sample blank with an optical density of 0·090. River B was a major tributary with a wide flow variation running through agricultural land; sample blank, 0·118–0·160. River C was a fast running river of moderate hardness originating as an upland stream; sample blank, 0·037. River D was a slow flowing river passing through agricultural land; sample blank, 0·112. A sample B-2 of river water B, abstracted during flood conditions, and a sample A-2 of river water A, to which was added bottom mud to give suspended solids at a level of 200–300 mg l^{-1}, were used to simulate the worst winter river conditions likely to be encountered. Concurrently, this biodegradation was also monitored in the presence of air but absence of airflow, which might simulate natural conditions more closely, for river samples A-2 and B-2 and these are designated A-3 and B-3.

For each of the glycols a series of 500-ml volumes of each river sample was prepared containing 0, 2 and 10 mg l^{-1} added glycols. These were allowed to stand in water baths at temperatures of 8 ± 0·5°C and 20 ± 0·5°C. A steady stream of moist air was passed over each solution in the series, a blank flask with deionized water being interposed between each series of flasks at different temperatures. Aliquots (5 ml) for glycol levels below 5 mg l^{-1} and 2 ml aliquots for levels above 5 mg l^{-1} were withdrawn from each flask after 1, 4, 7, 11 and 14 days and the glycol content determined. After 14 days the volume of solution remaining was measured and allowance made to the glycol content for evaporation or condensation. This follows the procedure adopted for a similar investigation of the biodegradation of urea (Evans *et al.*, 1973).

The degradation of isopropanol was not considered, since in our experience this deicing component is seldom encountered in airfield run-offs at temperatures >0 C, because of its volatility, and would not be expected in receiving surface waters.

RESULTS

The results of the biodegradation experiments are shown in Figs. 1–4.

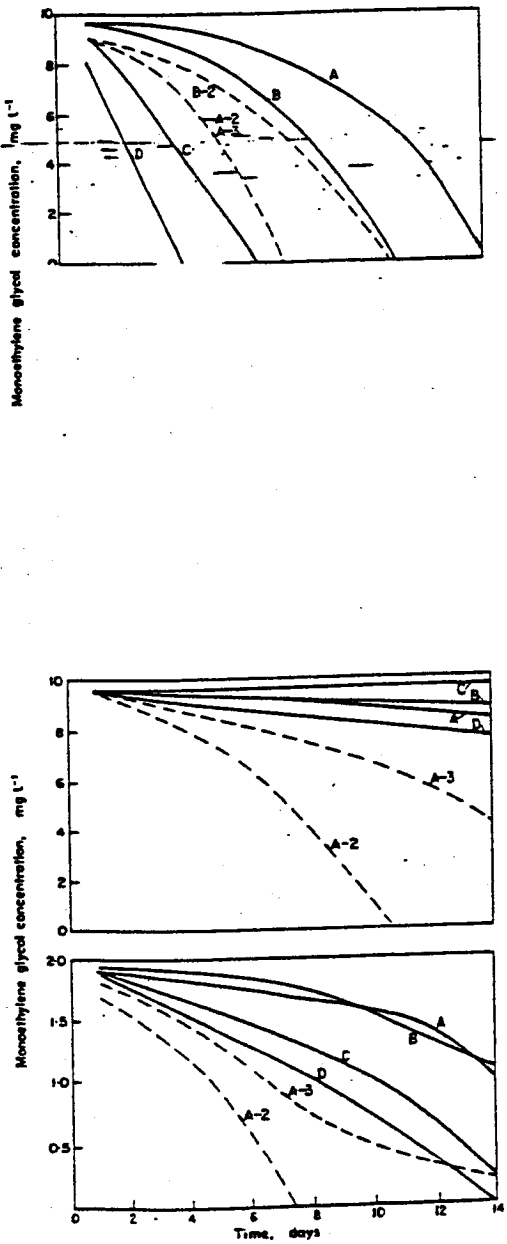

Fig. 2. Biodegradation of monoethylene glycol at 4 C in river water A, a major watercourse; river water B, a major tributary; river water C, a fast running river originating as an upland stream; river water D, a slow flowing river running through agricultural land; in samples A-2 and A-3, of river A with added bottom mud, and with and without aeration respectively; in samples B-2 and B-3 of river B, abstracted for flood conditions, with and without aeration respectively.

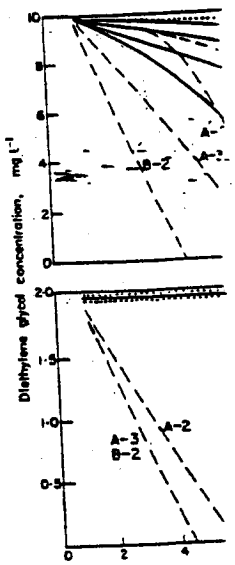

Fig. 3. Biodegradation of
8

Monoethylene glycol

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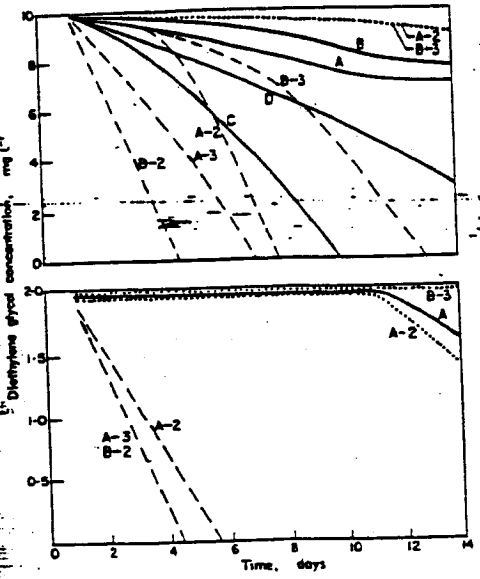

Fig.3. Biodegradation of diethylene glycol at 20 C ——— 8 C .....

Monoethylene glycol

Monoethylene glycol biodegraded completely within 3 days in all river waters tested at 20°C. After 1 day, levels remaining, at the 2 mg l^{-1} added glycol concentration, varied between 0 and 1·8 mg l^{-1}, while at the 10 mg l^{-1} added glycol concentration levels varied in the range 1·8–9·1 mg l^{-1}.

Biodegradation at 8°C was complete within 14 days for each of the river waters A–D (Fig. 1). The degradation in rivers A and B was gradual for the first 7 days but increased thereafter, irrespective of the concentration of glycol degraded in rivers A–D at a rate not exceeding after 11 days and breakdown was essentially linear and more rapid at the higher concentration. In river water A-2, with added bottom solids, and river water B-2, with high suspended solids, degradation occurred at an enhanced rate compared to rivers A and B. There was no difference between the breakdown characteristics of the glycol in river water when aerated, A-2, and in the presence of air but absence of aeration, A-3.

The degradation of monoethylene glycol at 4°C is shown in Fig. 2, and clearly indicates the reduction of bacterial activity as the temperature is lowered. The glycol degraded in rivers A–D at a rate not exceeding 0·2 mg l^{-1} daily irrespective of concentration. The rate of breakdown in river water A-2 was increased considerably, no glycol remaining after 7–10 days, but the presence of air only and absence of aeration, monitored concurrently, retarded this increased breakdown rate.

Di- and triethylene glycols

Variation in the biodegradation off diethylene glycol in river waters is illustrated in Fig. 3. Degradation, at at 20°C, was slow in river waters A and B, more rapid in river water D and complete in river water C within 10 days. The rate of breakdown in rivers C and D was the reverse of that found for monoethylene glycol. Samples of river waters with high suspended solids, A-2 and B-2, indicated that breakdown was virtually complete within 7 days, irrespective of the concentration of glycol present. A-3 and B-3, monitored concurrently in the presence of air but absence of aeration, showed a more rapid breakdown for A-3 while B-3 was retarded. At 8°C, diethylene glycol did not degrade in river water samples A-2 and B-3 within 11 days, and only slightly within 14 days.

Biodegradation of triethylene glycol (Fig. 4) was also dependent on the origins of the rivers. Thus degradation in river water A was variable at the levels tested, but in river waters B and C breakdown was at an apparent constant daily rate of 0·15 and 0·3–0·4 mg l^{-1} respectively. For river samples A-2 and B-2 breakdown was complete within 7–11 days and this rate was increased slightly for A-3 and B-3. At 8°C, in contrast to diethylene glycol, slight degradation of triethylene glycol occurred at a daily rate of 0·1 mg l^{-1} for river water samples A-2 and B-3.

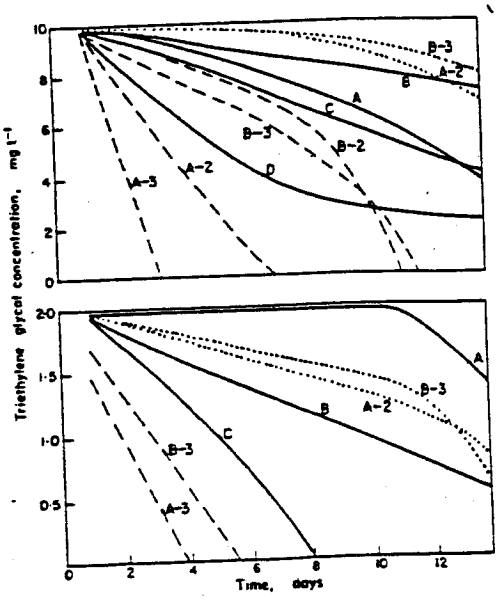

Fig. 4. Biodegradation of triethylene glycol at 20 C ——— 8 C .....

CONCLUSIONS

While monoethylene glycol biodegrades completely within 3 days at temperatures of 20°C, at lower temperatures bacterial activity is reduced. The variation in the rate of degradation at these lower temperatures suggests breakdown is dependent on the micro-organisms available and their population in individual rivers. At winter river temperatures (< 8°C) the evidence indicates monoethylene glycol may be degraded partially or completely within 7 days. The rates of biodegradation of diethylene glycol at 20°C are essentially similar to that of triethylene glycol. These rates are also dependent on the origin of the rivers with partial breakdown probable within 7 days, although total removal under certain conditions cannot be excluded. At lower temperatures (< 8°C) degradation is minimal for both glycols within 7 days.

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ISOLATION AND CHARACTERIZATION OF MICROTOX™-ACTIVE COMPONENTS FROM AIRCRAFT DE-ICING/ANTI-ICING FLUIDS

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ISOLATION AND CHARACTERIZATION OF MICROTOX™-ACTIVE COMPONENTS FROM AIRCRAFT DE-ICING/ANTI-ICING FLUIDS

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ABSTRACT

The primary goal of this project was to isolate and identify individual components from aircraft de-icing/anti-icing fluids (ADAF's) through a toxicity-based bioassay analysis. A Microtox™ bioassay-driven subfractionation scheme was used to isolate a number of active fractions from ADAF's. Active fractions were identified using multiple spectral techniques, including nuclear magnetic resonance, gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry and ultraviolet characterization. The primary Microtox-active fraction was shown to be a mixture of benzotriazole and tolyltriazoles, which are used as corrosion inhibitors in ADAF formulations. Spectral and toxicity confirmation were demonstrated through the use of commercially available standards.

Kewords: De-icing fluids, Anti-icing fluids, benzotriazole, tolyltriazole, toxicity

INTRODUCTION

Aircraft de-icing/anti-icing fluids (ADAF's) are used annually world-wide in considerable quantities to remove and prevent accumulation of snow, ice, and frost from aircraft. In Canada, it has been estimated that 8 million litres of ADAF's are used in a typical year [1]. At some airports, the amounts used and released into the environment are of such quantities that they must be reported under the Canadian National Pollution Release Inventory (NPRI). For example, Pearson International airport, near Toronto, reported environmental release of 464.9 tonnes of ethylene glycol in 1993, presumably as the result of deicing activities [2]. Because ADAF's contain between 50 and 90 percent ethylene, propylene or combinations of these or other glycols, Canadian Water Quality Guidelines for the management of storm water runoff from airports stipulate a 100 ppm (mg/L) level of total glycols as the allowable limit [3]. The primary justification for the establishment of this level is the increased biochemical oxygen demand (BOD) associated with high levels of glycols in water [4].

Recently, concern has shifted from the environmental effects of glycols to the possible environmental effects of other components found in ADAF fluids [5]. This concern has resulted from toxicological studies of complete ADAF fluids rather than the individual glycols [6,7]. Additional concerns have been raised in studies which have focused on the measurement of the effects of ADAF's in airport runoff during deicing events [8]. Chemicals, other than glycols, make up between 10 and 20 percent of de-icing/anti-icing fluids. These chemicals include wetting agents, corrosion inhibitors, surfactants, thickeners and other agents used to meet performance criteria established to ensure adequate de-icing/anti-icing of aircraft [4]. Unfortunately, the exact formulations of the ADAF's currently

in use are proprietary, making it difficult to relate environmental effects to the presence of specific chemical agents found in ADAF's. Because ADAF's have been found to have significant activity when measured by Microtox assays and, because of the difficulty in obtaining chemical compositions of the specific ADAF's in use, it was decided to undertake a Microtox-directed isolation to identify the potentially toxic components present in de-icing/anti-icing fluids. This paper describes the isolation and identification of a number of Microtox-active components found in de-icing/anti-icing fluids.

MATERIALS AND METHODS

Reagents

Milli Q™ (Bedford, MA) deionized water was used for all aqueous solutions. Acetonitrile, ethyl acetate, acetone and diethyl ether were all analytical grade (BDH, Toronto, Ont., Canada) and were used as received. Silica gel (100-200 mesh) was purchased from Rose Scientific (Calgary, Alb). Microtox bioassay reagents were from Microbics Corporation (Carlsbad, CA) and included: Microtox reagent (freeze-dried bacteria in vials and dilution water), Microtox osmotic adjusting solution (MOAS; 22% sodium chloride solution) and Microtox reagent diluent. 1H-benzotriazole, 5-methyl-1H-benzotriazole and 5,6-dimethyl-1H-benzotriazole hydrate were purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received.

ADAF's

Initial studies were undertaken on approximately 20 mL each of Type I and Type II fluids which had been used during the 1993/1994 deicing season. Subsequent studies were conducted on Type I and Type II ADAF's used in the 1994/1995 deicing season and were obtained from one of two major Canadian based airlines operating from Pearson

International airport. Approximately eight litres each of Type I and Type II was provided. In both cases, Type I was a viscous clear orange fluid while Type II was a viscous clear pink fluid. The fluids were stored at 4 °C until used.

Apparatus

GC-MS: Gas chromatographic analyses were performed on a Hewlett-Packard Model 5890 Series II gas chromatograph interfaced with a Hewlett-Packard Model 5790 mass selective detector. The column was a 30 m DB-5 capillary column (J&W Scientific) with a 0.25 mm inner diameter and a 0.25 μm film thickness. Ultra high purity (99.999%) helium was used as the carrier gas with the head pressure set at 7 psi. The injector was set at 250 °C and was run in the splitless mode with a delay of 0.7 minutes. The temperature program was 80 °C for two minutes then 5 °C/min to 280 °C. Full scan electron impact spectra were obtained scanning between 50 and 500 amu.

LC-MS and LC-MS/MS: LC-MS/MS studies were conducted at NovaMann International using a SpectraPhysics P200 liquid chromatographic pumping system interfaced with a Sciex API III-plus MS/MS system. The mobile phase was (70:30) acetonitrile/0.5mM ammonium acetate with 0.6% acetic acid at a flow rate of 250 μL/minute and an injection volume of 20 μL. The column was a Waters Bondapak TM reverse phase (3.9 mm x 300 mm) with a 10 μm particle size. Both a heated nebulizer and ionspray interface were used with nebulizer pressure at 97 psi and nebulizer heater at 55 °C. Samples were analyzed in both the positive and negative ion modes. Samples were also derivatized with BSTFA (N,O-bis(trimethylsilyl)-trifluoroacetamide), a derivatizing agent used to detect the presence of oxygen or nitrogen containing groups through the formation of the O-Si$(CH_3)_3$ or N-

$Si(CH_3)_3$ derivatives.

NMR: ^1H Nuclear Magnetic Resonance studies were conducted at the McMaster University Nuclear Magnetic Resonance Facility using a Bruker DRX-500 spectrometer. All samples were dissolved in $CDCl_3$ containing 1 % tetramethylsilane (TMS).

LC-Photodiode Array: A Waters 600E multisolvent delivery system and controller equipped with a Waters 990 photodiode array detector and Waters 715 Autosampler was used. For the preparative scale analysis, a Waters μBondpak™ reverse-phase column (300 mm x 3.9 mm i.d., 10 μm particle size) and 15 μL injection volume was used with a flow rate of 0.25 mL/min (70:30 acetonitrile:water). For the analytical scale analysis, a Biophase ODS column (250 mm x 4.6mm i.d., 5 μm particle size) with a flow rate of 1.0 mL/min (80:20 acetonitrile:water).

Microtox: Microtox analysis was conducted following the Basic Test Method recommended by Microbics Corporation and described elsewhere [9] .

Elemental analysis: Elemental analysis of both Type I and Type II were conducted following the procedures described elsewhere [10]

Preparative-Scale ADAF Liquid Chromatographic Separation and Bioassay Testing

Because of the small amounts of ADAF obtained during the 93/94 deicing season, (approximately 20 mL each of Type I and Type II) initial separations were undertaken using preparative scale high performance liquid chromatography (HPLC) followed by photodiode array detection. Initially, five major chromatographic peaks were observed over the 20 minute analysis time. The total analysis time was divided into eight major divisions varying

in length from one to five minutes each. An automated sample collector was used to collect fractions from each division. Fifteen microlitre aliquots were injected with each chromatographic run for a total of 3 mL (approximately 3 g) of the Type I solution. Individual fractions were reanalyzed and fractions showing similar chromatographic response pooled. The pooled fractions were then concentrated under nitrogen, and re-dissolved in 0.5 mL methanol. 100 microlitres of each was then taken and diluted into 5 mL of water and analyzed using the Basic Microtox Test Method, with the gamma values (Γ) being used to compare relative toxicity. Of the eight fractions collected, fractions 2 and 7 were shown to have significant Microtox activity relative to pure Type I ADAF (Table 1). Samples of the active fractions were submitted for nuclear magnetic resonance and liquid chromatography-mass spectrometric analysis. Both NMR and LC-MS analysis showed the fractions to contain multiple components although there was insufficient quantity for complete analysis.

Large-Scale ADAF Chromatographic Separation and Bioassay Testing

Approximately eight litres of both Type I and Type II ADAF fluids in use during the 94/95 deicing season were obtained for analysis. LC analysis of the mixtures showed similar chromatographic patterns to those obtained from ADAF's used during the 93/94 season. The initial fractionation scheme was developed using 10 mL of either Type I or Type II ADAF, with chromatographic retention times from the previous years study used as an aid to target the toxic fractions. Once it was determined that the scheme could be used to chromatographically match the Microtox active fractions from the previous years studies, the scheme was scaled up to one litre ADAF (Figure 1). The ADAF was acidified to a pH of 1 with a 6 M sulphuric acid solution and extracted three times with 500

mL ethyl acetate. Both the water and ethyl acetate fractions are further extracted according to the scheme in Figure 1 to produce 5 separate fractions (I-V). The ethyl acetate fraction was extracted with water to remove dissolved ethylene or other glycols. Each of these fractions was then analyzed by HPLC and Microtox, with fraction I chromatographically matching that of fraction 7 in Table 1. Fraction I also generated the most toxic response for Type I ADAF (Table 2). Fraction I was then applied to a silica gel column (300 mm x 24 mm, 100-200 mesh) and eluted with a gradient from 100% n-hexane to 50:50 diethyl ether:n-hexane. Fractions were again collected and analyzed by HPLC. The fraction eluting at 40% diethyl ether in hexane was shown to match the major HPLC peak from the previous studies. Analysis by LC with photodiode array detection showed this fraction to be relatively pure. The sample was characterized further by proton NMR, LC-MS/MS, GC-MS, and LC-photodiode array analysis.

RESULTS

Chemical characterization

Data from each spectral analysis is presented in Table 3. LC-MS/MS, GC-MS, and NMR showed the collected fraction to contain a mixture of isomers. GC-MS analysis showed the presence of three major components, two of the components (63 and 33% by area) having base peaks of ion mass-to-charge ratio (*m/z*) of 133 with the other component (6% by area) containing a (*m/z*) 119 base peak. The base peaks for each component were determined to be the molecular ions through MS/MS analyses providing evidence that the molecules contained one or three nitrogen atoms. The spectrum of each peak showed similar fragmentation patterns with major ions appearing at (*m/z*) 104, 77,

78, and 52 for the compounds with the base-peak of 133 and (m/z) 91, 64 and 52 for the compound with the base peak at 119. Proton NMR analysis provided evidence of a substituted aromatic compound by the presence of multiple signals between 7.8 and 7.1 ppm. Ultraviolet analyses showed an absorbance at 280 nm, characteristic of an azo type compound having at least 2 nitrogen atoms. As two nitrogen atoms would generate an even molecular weight by MS, the molecule must contain three nitrogen atoms giving it the molecular formula of $C_7H_7N_3$ (mw 133) and $C_6H_5N_3$ (mw 119). The identity of two of the compounds were confirmed as 1H-benzotriazole (6% of the area by GC-MS) and 5-methyl-1H-benzotriazole (33 % of the area by GC-MS) through the analysis of authentic standard material (Figure 2). The third compound (63% of the area by GC-MS) is tentatively identified as an isomer of the 5-methyl-1H-benzotriazole, with the most probable isomer having the methyl group substituted at one of the other positions on the aromatic ring rather than the 1-methyl benzotriazole isomer. This conclusion is supported by the compounds reaction with BSTFA and the formation of the subsequent *m/z* 205 derivative identified by MS. If the methyl group were bound to the N group, BSTFA would not have formed the derivative. It should be noted that benzotriazoles containing methyl groups on the aromatic ring are known as tolyltriazoles (Figure 2). HPLC analysis of Type II ADAF also confirmed the presence of benzotriazole and tolyltriazoles.

DISCUSSION

Canadian Water Quality Guidelines for the release of aircraft de-icing/anti-icing fluids into the aquatic environment have stipulated a 100 ppm total glycol limit [3]. This limit was assumed to be adequate for the protection of aquatic species under the Federal Fisheries

Act [11] and was based on the toxicity of glycols to specific aquatic organisms. Recent studies have raised issues relating to the potential toxicity of ADAF's independent of the glycol concentration [6-8]. Studies on actual ADAF's as well as airport runoff collected after deicing events have shown significant levels of toxicity [6-8].

The National Laboratory for Environmental Testing (NLET) has undertaken a bioassay-driven isolation and characterization of ADAF's using Microtox™ testing to identify potentially toxic components. Results from this work have shown that a class of corrosion inhibitors, identified as benzotriazole and tolyltriazoles, are the major Microtox-active constituents. Confirmation of the active components was accomplished through multi-spectral analyses and comparison with standard material. The identification of lesser Microtox-active fractions is still underway.

Benzotriazoles are commonly used as corrosion inhibitors and have found use in a number of applications such as with automobile antifreeze mixtures. Previous studies on the toxicity of benzotriazoles have shown that 1H-benzotriazole has a hazard rating of level 3 (HR3), the highest hazard rating assigned (LD_{50} <400mg/kg) [12]. Other work has shown benzotriazole to be a moderately toxic material [13,14]. Recommendations of a 0.1 mg/L value as the maximum permissible concentration of benzotriazole in water reservoirs have been proposed [15]. Studies on the exposure of workers through workplace air recommended a maximum permissible concentration of 10 mg/m^3 [16]. Microtox analysis of the mono and dimethyl substituted benzotriazoles, both of which have been shown to be present in ADAF's, showed increasing toxicity with increasing methylation (Table 4).

The presence of benzotriazoles as well as other potentially toxic constituents in

ADAF's suggests that the management of airport runoff and disposal of collected ADAF's be reevaluated to include possible environmental effects of additives. As azo compounds are known to biotransform under anaerobic conditions, conditions which develop from the biodegradation of glycols, into compounds with greater toxicity [17], studies should be conducted on the fate and effects of these materials in aquatic systems. These studies need to address issues related to the analyses of these compounds in both sediments and water. An additional question to be addressed is that of occupational exposure to ADAF's. Requirements vary as to the level of protective clothing, including respirators, which personnel involved in deicing are required to wear. As such, efforts should be made to evaluate worker exposure to ADAF's.

The presence of a variety of metals in ADAF's (Table 5) may also pose significant environmental impacts although the present study has not shown any correlation between metals and toxicity. It has been estimated that approximately 3785 litres of ADAF are used to deice a typical large passenger jet [4]. Depending on the flight activity at a particular airport and the efficiency with which the ADAF's are collected after use, this could equate to significant amounts of ADAF being released into the environment. As such, effects of metals and other constituent components from the use of ADAF's should also be addressed in future studies on the environmental effects of ADAF's.

The National Laboratory for Environmental Testing is currently working to determine the concentrations of benzotriazoles present in airport runoff and in sediments exposed to runoff from de-icing/anti-icing events.

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List of Tables

Table 1. Microtox gamma (Γ) values for liquid chromatographic fractions of Type I aircraft de-icing fluid.

Fraction	5 min Γ(5,15 °C)	15 min Γ(15,15 °C)
1	0.059	0.058
2	0.322	0.295
3	0.134	0.184
4	0.136	0.164
5	0.012	-0.030
6	0.154	0.108
7	0.248	0.220
8	0.069	0.027
Type I ADAF	0.305	0.233

Table 2. Microtox gamma values of the liquid/liquid extracts of Type I aircraft de-icing/anti-icing fluids (see Figure 2 for extraction scheme).

Extract	5 min Γ(5,15 °C)	15 min Γ(15,15 °C)
I	>999	**
II	0.919	0.933
III	0.493	0.483
IV	-0.018	-0.052
V	0.158	0.124
Type I ADAF	4.689	6.089
Phenol Standard (45mg/L)	2.948	3.131

** 0 transmission of light.

Table 3 a. GC-MS Data of Microtox-active fraction from Type I ADAF.

	Retention Time(min)	Ion Mass(abudunance)
FI	16.64	119(100), 91 (90),64(84), 63(68), 52(24)
	18.45	133(73), 104(100), 78(38), 77(41), 52(22), 51(30)
	19.41	133(61), 104(100), 78(32), 77(43), 52(18), 51(24
1H-benzotriazole	16.64	119(100), 91(80), 64(90), 63(68), 52(32)
5-methyl-1H-benzotriazole	19.41	133(58), 104(100), 78(35),77(43), 52(24), 51(29)
5,6-dimethyl-1H-benzotriazole	22.75	147(54), 132(21), 119(27), 118(100), 104(27), 91(60), 77(14), 65(23), 52(15)

Table 3 b. LC-UV Data of Microtox-active fraction from Type I ADAF.

	Retention time(min.)	UV λmax.(nm)*
FI	6.94	208, 270, 290
	11.49	208, 270, 290
	12.25	208, 270, 290
1H-benzotriazole	RT=6.94	208, 270, 290
5-methyl-1H-benzotriazole	12.25	208, 270, 290
5,6-dimethyl-1H-benzotriazole	22.42min	208, 270, 290

*: mobile phase is 20% acetonitrile in water.

Table 4. Microtox EC50 values for benzotriazole standards and isolated benzotriazoles from Type I ADAF.

Compound	N	EC50 (5 min) Mean ± S.D. (mg/L)	EC50 (15 min) Mean ± S.D. (mg/L)
1H-benzotriazole*	3	41.13 ± 4.63	41.65 ± 11.01
5-methyl-1H benzotriazole*	3	5.69 ± 1.19	5.91 ± 1.11
5,6-dimethyl-1H-benzotriazole	3	0.72 ± 0.28	0.80 ± 0.33
Isolated Fraction from ADAF (Type I)	3	11.08 ± 0.49	12.39 ± 2.25
Phenol Standard	6	21.83 ± 3.98	20. 59 ± 6.20

* Identified in Type I ADAF and Type II ADAF.

Table 5. Trace metal analysis of Type I and Type II ADAF.

ELEMENT	TYPE I (mg/L)	TYPE II (mg/L)
Al	ND	0.46
Ba	ND	0.042
Be	ND	ND
Ca	3.4	1.2
Cd	1.5	ND
Co	0.018	0.024
Cr	0.016	0.006
Cu	0.552	0.084
Fe	39.078	12.498
K	42.8	221.6
Li	0.018	0.036
Mg	1.0	1.2
Mn	0.478	0.262
Mo	0.01	ND
Ma	141.2	85.0
Ni	ND	0.034
Pb	9.836	ND
Sr	0.02	0.01
V	ND	ND
Zn	5.272	3.272

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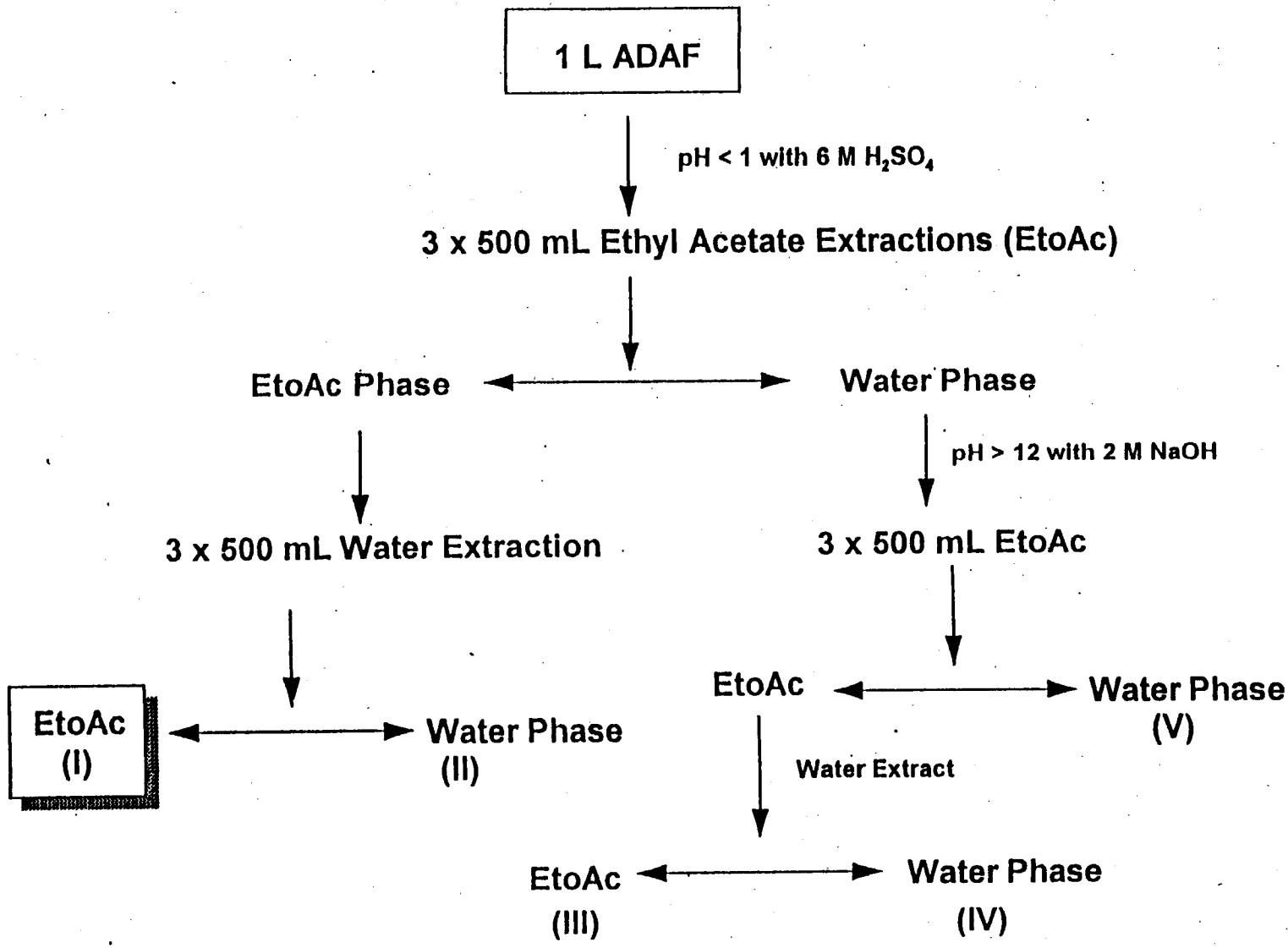
1 L ADAF
pH < 1 with 6 M H_2SO_4
3 x 500 mL Ethyl Acetate Extractions (EtoAc)
EtoAc Phase
Water Phase
pH > 12 with 2 M NaOH
3 x 500 mL Water Extraction
3 x 500 mL EtoAc
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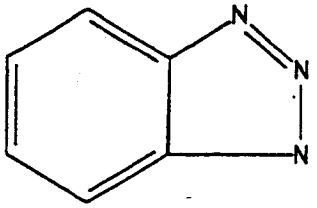
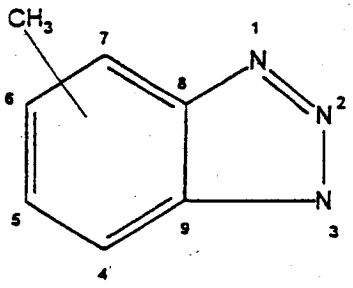
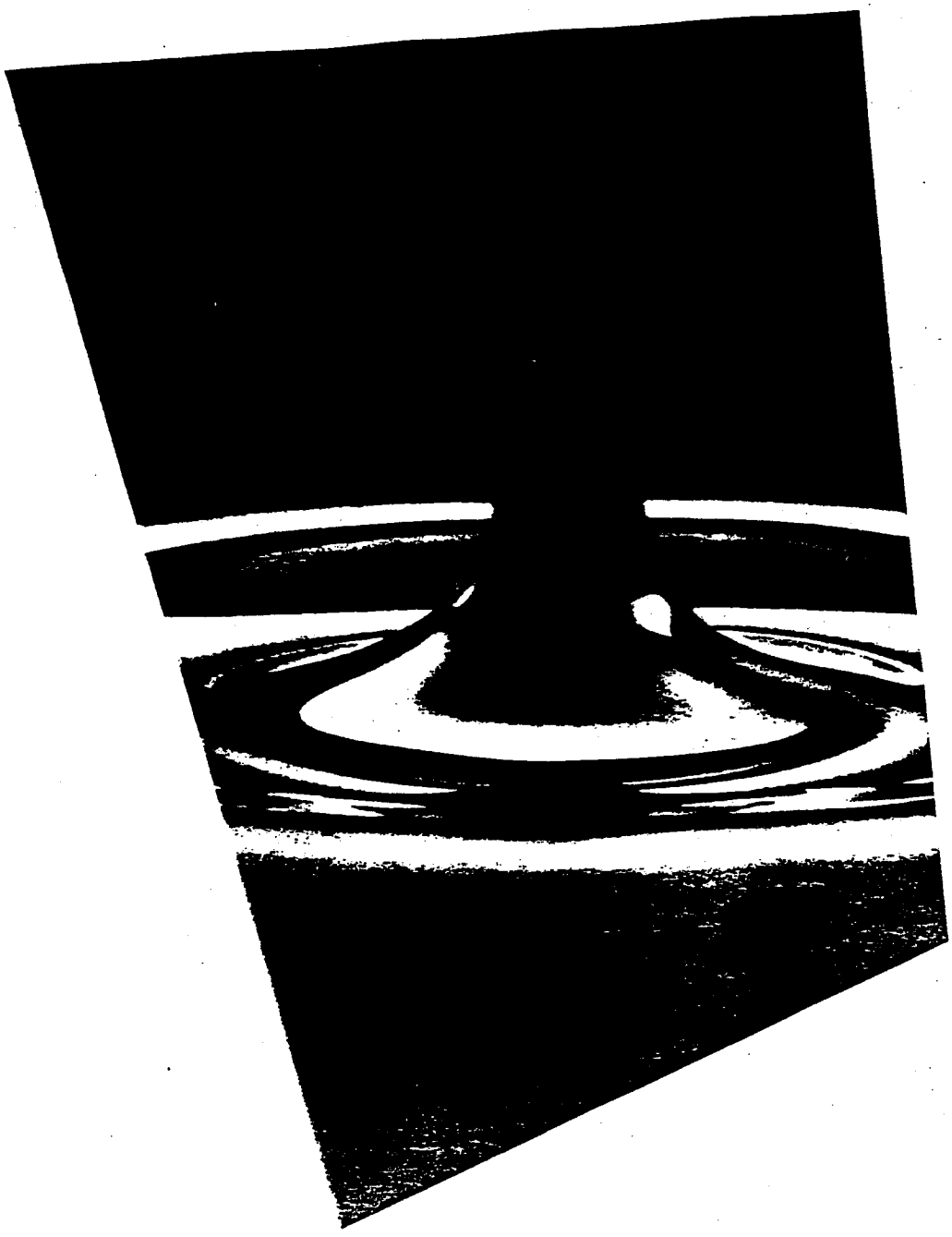


BENZOTRIAZOLE (I)



TOLYLTRIAZOLE (II)

PURITY PLUS



DOW PROPYLENE GLYCOL USP

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THE PLUS IN PURITY PLUS

Propylene Glycol USP is a high purity product that helps assure quality and desired performance in foods, beverages, cosmetics, pharmaceuticals and a variety of other low-toxicity applications. The added PLUS, however, comes from knowing that it's backed by Dow — so you can be assured of outstanding quality and unsurpassed reliability.

THE DOW COMMITMENT. At Dow, we are committed to the propylene glycol business. Since we first began manufacturing propylene glycol in 1948, propylene glycol has always been one of our key strategic businesses and therefore we are dedicated to maintaining our position as the leading global producer.

GLOBAL SUPPLIER. Today Dow is the world's leading propylene glycol producer with an annual global capacity in excess of *700 million pounds*. With two of the manufacturing sites in the United States and multiple distribution centers, you can be confident in knowing that Dow can deliver product when you need it, where you need it.

KEEPING COSTS LOW. Being the leading producer means we are a cost-effective supplier. Our propylene glycol production is fully integrated into other company businesses, which allows Dow to successfully maintain our position as a low-cost producer.

CUSTOMER SATISFACTION. At Dow, customer satisfaction goes beyond offering our customers an outstanding product. We also provide them access to a wide variety of resources and reference materials. For example, our Sales, Technical Service & Development (TS&D), Research & Development and Quality Assurance groups all provide continuous customer support. As part of our commitment to Responsible Care,® Dow provides vital health and safety information through presentations, literature, up-to-date Material Safety Data Sheets and formulation information.

PRODUCT QUALITY. At Dow, we employ rigorous quality control procedures — the best in the business. In order to maintain United States Pharmacopeia (USP) grade status, Dow adheres to the Good Manufacturing Practices guidelines that govern every aspect of production and shipment of U.S. Food and Drug Administration (FDA) regulated products. And to make sure that product integrity is maintained at the distributor level, Dow offers ongoing white room drumming support, including start-up assistance and thorough white room inspections.

® Registered Service Mark.

A VERSATILE INTERMEDIATE. Propylene Glycol USP is an excellent solvent for many water-insoluble organic chemicals. It is a clear, colorless, slightly viscous liquid which is completely miscible in water. Because Propylene Glycol USP displays so many different properties, it has become the product of choice for cosmetic, food and pharmaceutical industries. Some of its more common applications include:

- An important solvent for aromatics in the flavor concentrate industry.
- A wetting agent for natural gums.
- A solvent in elixirs and pharmaceutical preparations containing some water-soluble ingredients.
- A coupling agent in the formulation of sunscreen lotions, shampoos, shaving creams and other similar products.
- A low temperature heat-transfer medium in brewing and dairy cooling systems and in other refrigeration equipment having cooling coils which are in direct contact with beverages.
- In aqueous solution, it displays excellent antifreeze properties.
- A humectant in tobacco.
- A foam stabilizer in shaving creams.
- A solvent for printing inks.
- A solvent and coupling agent in many other applications.

At Dow, we are committed to providing our customers with nothing less than the best. Quality and purity are assured in every shipment of Propylene Glycol USP. And our dedication to product stewardship helps ensure safe and responsible use of this product.

ADVANTAGES OF DOW PROPYLENE GLYCOL USP

EXCELLENT SOLVENT ACTION. Propylene Glycol USP is completely miscible with water and many organic materials such as alcohols, esters, ethers, aldehydes, as well as many natural vegetable and animal fats and oils. This property is very beneficial in solubilizing and stabilizing products for cosmetics and foods.

LOW TOXICITY. The low toxicity of Propylene Glycol USP is unique among the glycols and is what permits it to be used as a direct additive in foods and drugs.

MEETS U.S. FOOD AND DRUG ADMINISTRATION STANDARDS. To maintain USP grade status, Dow Propylene Glycol USP is manufactured to the specifications of the U.S. FDA and thus is approved as a multiple purpose substance for direct addition to a number of foods and as a pharmaceutical aid in drug formulations.

HUMECTANT ACTION. Propylene Glycol USP has the ability to obtain and hold water in a product. It is one of the most effective materials approved for foods as a humectant, and is superior to other compounds such as sorbitol and mannitol in its ability to hold water.

PLASTICIZING AND SOFTENING. Propylene Glycol USP can plasticize or soften a material. This is possible because of its moderate viscosity, wetting properties, low volatility and compatibility with many compounds.

ODOR, COLOR, TASTE. Dow Propylene Glycol USP is odorless, colorless and has the characteristic taste of pure propylene glycol. These properties enhance its use in products because it can perform its intended function without impacting other features of the product.

LOW VOLATILITY. The vapor pressure of propylene glycol is 0.08 mm Hg at 20°C. Low volatility is a desirable feature in formulation of products to meet low VOC regulations.

AVAILABILITY. The Dow Chemical Company produces Propylene Glycol USP in worldscale plants in Freeport, Texas and Plaquemine, Louisiana. Dow terminals are located across North America.

QUALITY CONTROL. Dow Propylene Glycol USP is manufactured using modern computer controlled plants. Statistical Quality Control (SQC) and Statistical Process Control (SPC) methods are used to ensure that product quality consistency is always maintained.

Applications In The Food Industry

Propylene glycol is one of four polyhydric alcohols often found in foods. Compared to the other three (glycerine, sorbitol and mannitol), propylene glycol is preferred when low viscosity, high hygroscopicity, good oil solvency or complete miscibility with water is desired. It does not contribute to product sweetness as do the other alcohols.

Polyhydric alcohols are used in foods to help retain the original quality of the food or to modify the original quality or texture of the product. Propylene glycol can be effective in acting as a 1 crystallization modifier, 2 humectant, 3 softening agent, 4 solvent, 5 viscosity agent, 6 rehydration aid or 7 dietary agent.

Direct Food Additives

Flavor solutions and emulsions. The efficacy of Propylene Glycol USP as a solvent for flavoring materials is shown in Table 1. A close look at this table reveals that the only important class of raw materials not sufficiently soluble in Propylene Glycol USP for the practical preparation of flavor solutions is the citrus oils. However, by using edible wetting agents, colloidal suspensions of these oils may be prepared which, for all practical purposes, are the same as solutions. This is an example of where propylene glycol serves as a coupling agent to enhance the stability of a system. It is common for flavor concentrates to contain 15-30% propylene glycol, and the U.S. FDA allows up to 97% propylene glycol in this application.

TABLE 1

SOLUBILITY OF FLAVORING MATERIALS IN PROPYLENE GLYCOL WATER MIXTURES AT 77°F (25°C)†

Flavoring	Percentage Propylene Glycol				
	100%	80%	60%	40%	20%
	Solubility in Fluid Ounces per U.S. Gallon of Solvent (Metric conversion: value x 7.8 = ml/liter)				
Alcohol C-10	∞	∞	0.52	0.07	0.03
Alcohol C-12	∞	1.29	0.16	<0.03	<0.03
Aldehyde C-16	∞	2.89	0.10	0.06	0.05
Allyl Butyrate	45.37	10.35	2.32	0.95	0.50
Allyl Caproate	20.87	3.00	0.49	0.06	0.04
Amyl Acetate	∞	∞	∞	2.33	1.99
Amyl Butyrate	18.25	3.07	0.63	0.25	0.08
Iso Amyl Formate	∞	8.34	7.20	2.60	2.55
Amyl Valerianate	12.04	2.50	0.42	0.12	0.07
Anethol	7.04	0.89	0.34	0.05	<0.03
Benzaldehyde	∞	29.84	6.09	2.32	1.00
Benzyl Acetate F.F.C.	∞	10.75	2.55	0.53	0.35
Benzyl Propionate	∞	5.30	1.02	0.31	0.14
Cinnamic Aldehyde (99-100% pure)	∞	2.24	0.39	0.07	0.03
Citral	∞	0.45	0.30	0.15	0.06
Diacetyl (100%)	∞	∞	∞	∞	26.79
Ethyl Butyrate	∞	17.08	4.76	0.43	0.11
Ethyl Acetate	∞	∞	∞	19.03	12.79
Ethyl Cinnamate	22.96	3.99	0.59	0.10	0.04
Ethyl Formate	∞	∞	∞	∞	30.01
Ethyl Oxyhydrate (Conc. special colorless)	∞	∞	∞	∞	4.46
Ethyl Valerate	38.30	11.10	3.51	1.06	1.04
Eucalyptol	35.70	7.16	2.52	0.58	0.43
Eugenol USP	∞	—	49.2	0.16	0.06
Maltol	5.89	5.28	4.28	3.14	2.27
Methyl Anthranilate	∞	30.8	4.14	0.57	0.45
Methyl Cyclopentenolone	24.07	23.00	18.86	10.83	6.02
Methyl Salicylate	24.50	4.79	1.14	0.34	0.22
Nutmeg Oil	0.73	0.446	0.25	0.21	0.14
Ocotea Cymbarum	11.58	1.46	0.25	<0.03	<0.03
Oil Anise, Star ISP	3.81	0.80	0.26	0.06	0.03
Oil Bay	1.24	0.23	0.07	0.03	<0.03
Oil Bay (Terpeneless)	∞	4.36	0.17	0.06	0.03
Oil Caraway	3.59	0.71	0.06	0.04	0.04
Oil Cassia	∞	4.06	1.01	0.89	0.25
Oil Cassis (Terpeneless)	∞	6.75	1.15	0.13	0.07
Oil Cloves	∞	1.53	0.38	0.25	0.12
Oil Cloves (Terpeneless)	∞	2.88	0.04	0.05	0.04
Oil Dill Weed	1.71	0.06	0.04	<0.03	<0.03
Oil Ginger	<0.03	—	—	—	—
Oil Lemon	1.25	0.78	0.47	0.28	0.05
Oil Lime (Distilled)	2.34	0.23	0.24	0.03	<0.03
Oil Mace (Distilled) (So Called)	1.605	0.42	0.07	0.04	0.03
Oil Peppermint	∞	0.40	0.06	0.03	<0.03
Oil Peppermint (Terpeneless)	∞	0.73	0.07	0.04	0.04
Oil Petitgrain (Terpeneless)	∞	0.98	0.17	0.06	0.03
Oil Pimento Leaf	∞	1.24	0.21	0.08	0.04
Oil Sage (Spanish)	2.42	0.28	0.14	0.06	0.03
Oil Sassafras	2.50	1.56	0.25	0.15	0.10
Oil Spearmint, (N.F. XV)	1.07	0.06	0.05	0.03	0.03
Oil Thyme, White (High Test)	∞	1.35	0.31	0.10	<0.03
Oil Wormseed (American Chenopodium)	13.46	1.07	0.16	0.06	0.04
Oleo Resin Celery	0.15	0.05	<0.03	<0.03	<0.03
Oleo Resin Ginger	Immisc.	—	—	—	—
Oleo Resin Pepper	Immisc.	—	—	—	—
Orange Oil	0.20	0.21	0.13	0.09	0.05
Phenethyl Alcohol	∞	∞	∞	30.80	4.10
Phenethyl Formate	26.20	4.47	0.71	0.18	0.04
Phenethyl Propionate	∞	8.55	1.21	0.42	0.25

†The solubilities of over 100 additional essential oils and aromatic chemicals are listed in D.D. Laiotz, American Perfumer 48, No. 11, 64, 69 (1946).

∞ = Miscible or soluble in all proportions.

Immisc. = Immiscible or completely insoluble.

< = Less than.

FLAVOR EXTRACTOR OR PROCESSING AID. Propylene glycol is used as a solvent in the extraction of vanilla flavor from vanilla beans and coffee flavor from roasted coffee. In addition, the high solubilizing power of this glycol permits it to be utilized in the extraction of many other natural flavoring materials. It is also used to extract fat from cocoa powder.

HUMECTANCY AND REHYDRATION. Propylene glycol is the best choice of the polyhydric alcohols for providing moisture balance or humectancy. It is particularly effective for low moisture foods and is widely used in processed fruits and vegetables such as shredded coconut and in the bakery industry for packaged pastries. Table 2 gives the equilibrium values for water-propylene glycol solutions at various relative humidities. This information can be used to estimate the humectancy value of propylene glycol in a product.

TABLE 2

HUMECTANT VALUES OF PROPYLENE GLYCOL†

Temperature of Air		Relative Humidities								
°C	°F	10%	20%	30%	40%	50%	60%	70%	80%	90%
−6.7	20	96.8	91.4	90.0	84.6	77	73	68	55	40
4.4	40	97.0	92.3	90.2	85.2	78	74	68	55	40
15.6	60	97.1	92.9	90.4	85.8	80	74	68	55	40
26.7	80	97.1	93.5	90.5	86.3	81	75	68	55	40
37.8	100	97.2	93.9	90.6	86.6	82	75	68	55	40
48.9	120	97.2	94.3	90.7	86.7	83	76	68	55	40

† Values are given as percent by weight glycol in water solutions that will be in equilibrium with air of various temperatures and humidities.

Rehydration of dried foods is sometimes improved if a polyhydric alcohol has been used during the dehydration process. This avoids denaturalization of the protein and may reduce tendency of food cell structures to collapse.

FOOD COLOR SOLVENT. Propylene glycol is an excellent, widely used solvent for many edible food dyes. Its advantages over other solvents used for this purpose include lower volatility and improved resistance to light.

ANTIOXIDANT SOLVENT. Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propyl gallate are food antioxidants which are sold dissolved in propylene glycol. These antioxidants find use in a wide variety of both human and animal foods.

PLASTICIZER AND SOFTENING AGENT. In manufacturing the cork seals and crowns used with food and beverage products, it is necessary to incorporate a plasticizer to keep the cork pliable and in proper condition to seal the container. Since the food product will be in contact with the cork, a nontoxic plasticizer is required. Propylene glycol is also used in semi-dry foods, such as packaged cookies, as a softening agent to provide a better "mouth feel."

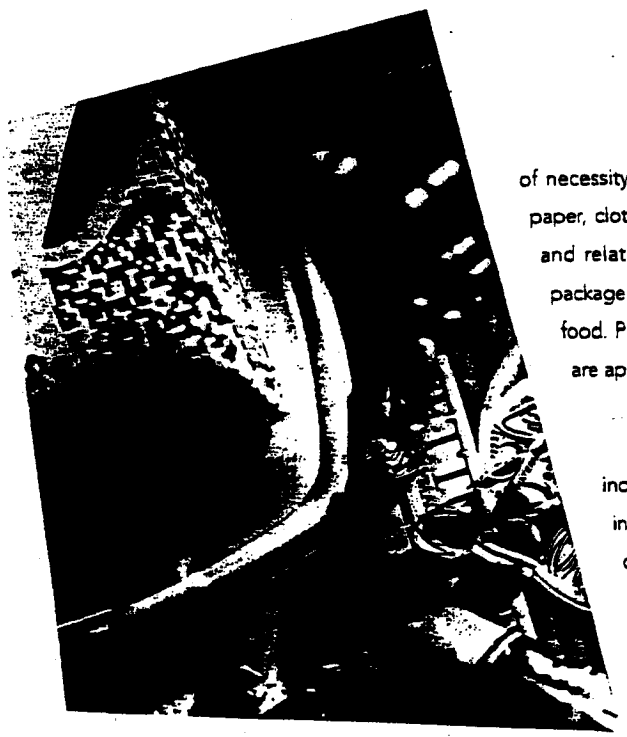
NUTRITIONAL VALUE. Since propylene glycol is often used in foods, its nutritional value is sometimes required for proper food labeling. Propylene glycol provides caloric value only as a food product. The value that should be used for calculating food label nutritional information is 570 kilogram calories (large Calories) per 100 grams.

ANIMAL FEED. Dow offers SIRLENE* feed grade propylene glycol as the glycol of choice for use in pet and cattle food. SIRLENE is a special trademarked brand of propylene glycol which meets the U.S. FDA 21CFR Part 582.1666 for use as an animal feed. In this application propylene glycol provides humectancy for moist and semi-moist products and is an excellent solvent and stabilizer for molasses-based liquid cattle feeds designed to reduce livestock stress during transport and to enhance weight gain in feedlots.[1]

Propylene glycol has been shown to be a very effective treatment for the control of ketosis in cattle[2] and SIRLENE is approved by the U.S. FDA for treatment of ketosis.

*Trademark of The Dow Chemical Company

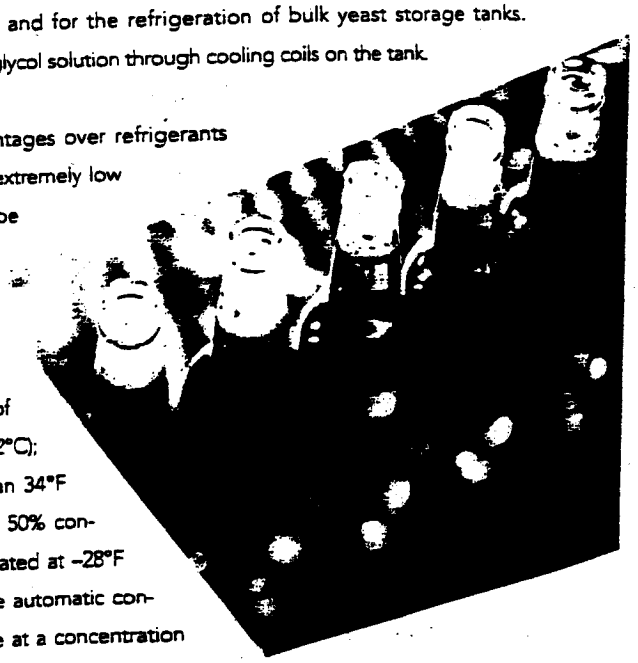
Indirect Contact Food Applications



PACKAGING AND INKS. Many food products are, of necessity, in relatively intimate contact with printed materials such as paper, cloth, etc. Standard printing inks based upon petroleum solvents and relatively odorous materials are not U.S. FDA approved in food package applications since they impart undesirable odor and taste to the food. Propylene glycol is an excellent solvent for highspeed inks which are approved for indirect food contact.

HEAT-TRANSFER MEDIUM. The food industry makes wide use of propylene glycol as a heat-transfer fluid in the brewing of beer, the processing of milk and the production of ice cream and other liquids. It is also the fluid often chosen for cooling food storage facilities and grocery store display cases.

In the brewing industry, propylene glycol is utilized to cool the tanks in which fermentation takes place and for the refrigeration of bulk yeast storage tanks. Cooling is accomplished by circulating a 30% aqueous propylene glycol solution through cooling coils on the tank.



Propylene glycol offers a number of advantages over refrigerants such as chilled water or calcium chloride brine. Because of the extremely low toxicity of the glycol, there is less risk that the product will be unusable if contamination has occurred through small leaks in the system. In the brewing of beer the presence of 0.25 to 0.50% propylene glycol has no effect on taste, and there is no significant effect on fermentation until the percentage of glycol reaches at least 5%. A 30% concentration of glycol permits coolant temperatures down to about 10°F (–12.2°C); in contrast, chilled water permits temperatures no lower than 34°F (1.1°C). For applications requiring even lower temperatures, a 50% concentration of propylene glycol can be used which can be operated at –28°F (–33°C). Propylene glycol also provides some lubrication for the automatic controls of the cooling system. Addition of dipotassium phosphate at a concentration of 1% provides a buffering action to help maintain a neutral pH and reduce corrosion.

Immersion freezing is a fast, efficient process for the quick freezing of poultry and other foods. Dow Propylene Glycol USP has a United States Department of Agriculture P1 listing for this application. Immersion freezing has noteworthy advantages over conventional freezing in that the freezing cycle time is greatly decreased. Freezer space requirements are reduced and plant flexibility is improved. The final color of poultry may be varied from white or flesh-colored to mahogany by adjusting the temperature of the freezing bath. In freezing poultry, the birds are sealed in a closely adhering air and water-tight bag before immersion in the freezing liquor. This tight package prevents skin blotching during freezing, dehydration after freezing and contamination of the product with the liquor.

For any heat transfer system, the propylene glycol solution may gradually become contaminated with glycol oxidation products, food particles, or various impurities from other sources. Periodic examination for low pH, excessive odor or discoloration will help determine when the solution is spent and must be replaced.

EQUIPMENT CLEANER. Propylene glycol can be used to prevent contamination of food processing equipment during periods of idleness. When cleaning processing tanks, pipelines, valves, etc., it is often impossible to remove the last traces of food materials. Unless preventative measures are taken, these food materials can subsequently spoil and contaminate future production.

After normal cleaning, a final rinse with propylene glycol will aid in preventing spoilage of residual traces of food because of its natural antimicrobial properties. Before the equipment is placed in service, the residual glycol can be removed easily by flushing with water.

APPLICATIONS IN COSMETICS

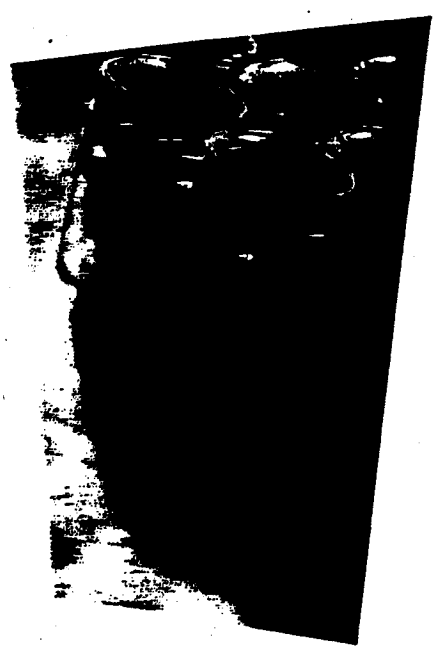
Dow Propylene Glycol USP is used as a carrier, emollient, softening agent, viscosity modifier and humectant in many types of cosmetics. It has been reported to be used in over 4,000 cosmetic products. It is an excellent solvent for many dyes and fragrances and helps to disperse ingredients. Water-in-oil emulsion stabilities can often be improved with the addition of propylene glycol as a co-emulsifier. The Cosmetic Ingredient Review Committee[3] has approved the use of propylene glycol at a concentration of up to 50% in cosmetic products.

Several general formulations for various types of cosmetic products which contain propylene glycol are presented herein. These are, however, only examples and the cosmetic formulator should refer to other sources such as *Flick's Cosmetic and Toiletry Formulations*[4] for additional formulation information or to textbooks such as Williams and Schmitt's[5] that discuss in detail the science of cosmetics.

ANTIPERSPIRANTS AND DEODORANTS. Roll-on and stick antiperspirant/deodorants now dominate this market and the current trend is toward clear gel products. Propylene glycol has replaced ethyl alcohol in many formulations because of the requirement for lower volatility, no odor, formulation stability and improved viscous properties.

CLEAR ANTIPERSPIRANT STICK[6]

Hexylene glycol	20.0%
Propylene carbonate	8.0
C_{12-15} alcohols benzoate	5.0
Dipropylene glycol	34.0
Dibenzaldehyde monosorbitol acetal	3.0
Aluminum chlorohydroxide	15.0
Propylene glycol	15.0



SKIN CARE PRODUCTS. Skin care products include hand and body moisturizers, facial moisturizers, suncare products and cleansers. Propylene glycol can be used in mild skin cleansers as a solvent and stabilizer for the surfactants.

In a typical oil-in-water (O/W) emulsion hand cream, propylene glycol helps to stabilize the emulsion and also acts to hydrate skin and relieve dryness. Anti-aging products containing collagen are designed to rejuvinate the dermis layer of the skin. The ability of propylene glycol to penetrate skin is thought to assist in making products that contain collagen more effective.

Protection from both UV-A and UV-B radiation is recognized today as equally important in preventing skin damage from the sun. The sunscreen formulation chemist will find that propylene glycol is a good solvent and co-emulsifier for many of the UV absorbers now available as shown in the example.

MILD SKIN CLEANSER[7]	
Lysine laurate	10.0%
Lysine myristate	10.0
Lauric acid	3.0
Propylene glycol	5.0
Water	Balance

OIL-IN-WATER HAND LOTION[4]	
Amerlate P	0.5%
Glyceryl monostearate	2.0
Stearic acid	3.0
Triethanolamine	1.0
Propylene glycol	5.0
Water	Balance

COLLAGEN CREAM[4]	
Cremophor A 11	3.0%
Luvitol EHO	5.0
Paraffin oil	5.0
Cetyl/stearyl alcohol	7.0
Propylene glycol	3.0
Collagen CLR	5.0
Water	Balance

SUNSCREEN[8]	
Tocopheryl isostearate	8.0%
Stearic acid	10.0
Stearyl alcohol	4.0
Glyceryl monostearate	2.0
Fragrance	1.0
Propylene glycol	10.0
Glycerin	4.0
Potassium hydroxide	0.4
Water	Balance

HAIR CARE PRODUCTS. Propylene glycol is found in many hair care products including shampoos, conditioners, thickeners, and styling gels. Solvency and stabilization are the most important roles that propylene glycol fulfills in these products. Propylene glycol is often added to the water phase for emulsion products as an aid to forming a stable final product.

OIL-FREE CLEAR HAIR RINSE[4]

Celquat SC-240	0.6%
Natrosol 250 HHR	0.8
Propylene glycol	3.0
dl-Panthenol	0.2
Germall 115	0.2
Methyl paraben	0.1
Water	Balance

LEAVE-ON CONDITIONER[5]

Cetyltrimethylammonium chloride	0.2%
Lactamide-MEA	1.2
Panthenol	1.2
Propylene glycol	2.0
Bromonitropropanediol	0.05
Water	Balance

APPLICATIONS IN PHARMACEUTICALS

In the preparation of a pharmaceutical the active ingredients must be solubilized in a base ingredient for effective use of the product. Because of its affinity for both hydrophilic and hydrophobic compounds and its proven safety, Propylene Glycol USP is a very effective formulation base for oral, topical and injection drug products. In addition to its solvency, Propylene Glycol USP also serves as an emollient and humectant, which are desirable features that aid in application and appearance of topical products.

Table 3 illustrates the scope of the solubilizing properties of Propylene Glycol USP and is helpful in formulating new drug products.

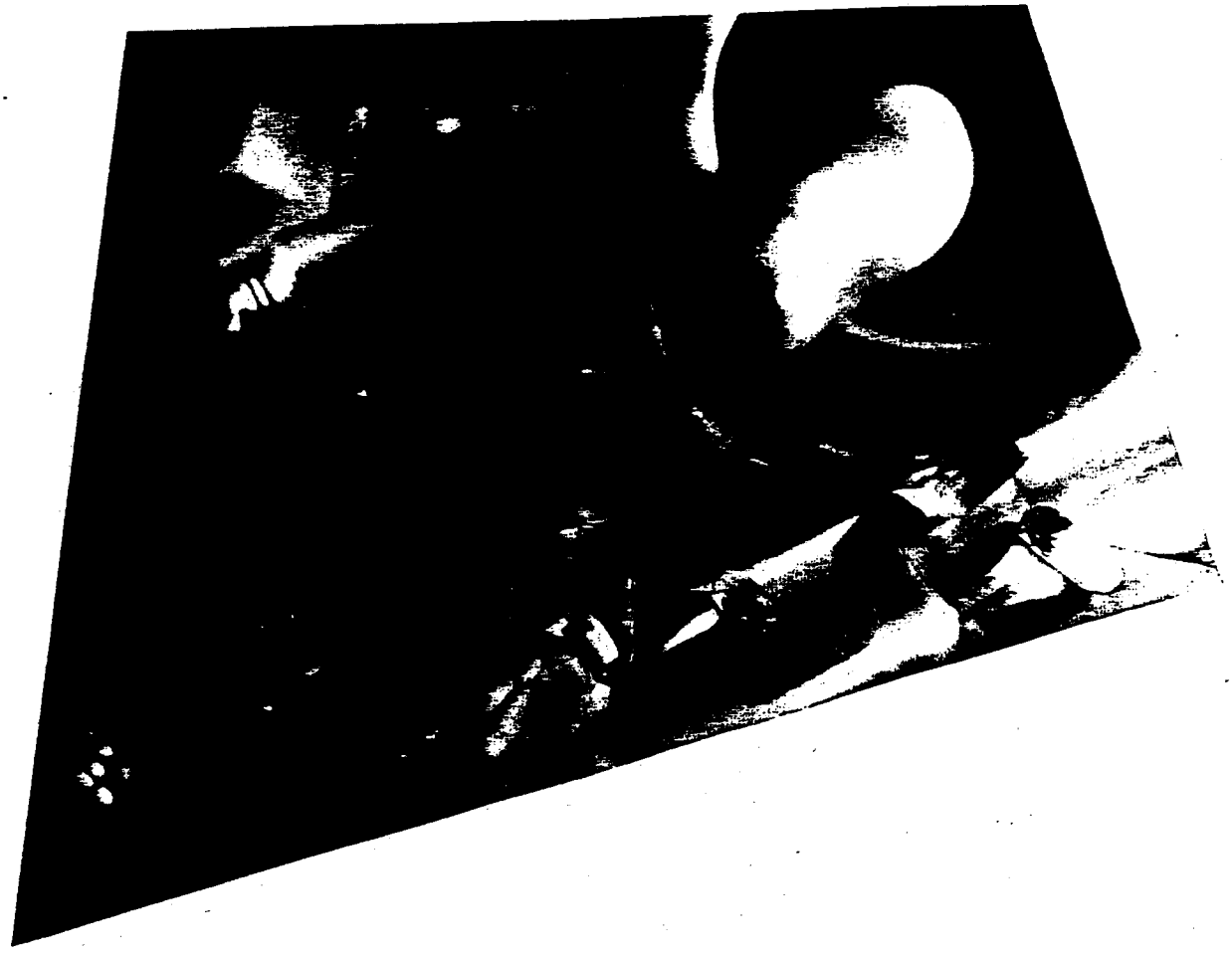


TABLE 3

SOLUBILITY OF PHARMACEUTICALS IN PROPYLENE GLYCOL USP — TEMPERATURE 25°F (–4°C)

Material	Percent Solubility
Drugs and Medicinals	
Acetanilide	2.09
Acetarsone	0.52
Acethophenetidine	2.10
Alion	4.37
Antipyrine	>55.00
Caffeine	0.77
Chloral Hydrate	>89.00
Ethyl Carbamate	>57.00
Glycine	<0.45
Hexamethylenetetramine	11.22
o-Hydroxybenzyl Alcohol	44.10
Paraldehyde	∞
Pepsin	<0.08
Phenobarbital (Luminal Sodium)	>49.00
Resorcinol	55.70
Sodium Bismuth Thioglycolate	9.40
Sodium Iodobismuthite	6.00
Sulfadiazine	0.30
Sulfanilamide	7.25
Sulfapyridine	0.50
Sulfathiazole	1.71
Terpin Hydrate	18.20
Urea	22.20
Local Anesthetics	
Benzocaine	12.20
Benzyl Alcohol	∞
Diothane	5.00
Salicyl Alcohol (Saligenin)	4.00
Antiseptics	
Camphor	9.80
Calcium Sulfocarbolate	>30.00*
Chlorothymol	70.00
Hexylesorcinol	>80.00*
Menthol	>50.00
Merthiolate	>29.00
Antiseptics, con't.	
Metaphen	<0.27
Salol	10.50
Thymol	>50.00
Trichloro-tert-butanol	>60.00
Zinc Sulfocarbolate	>39.00
Vitamins and Hormones	
α Estradiol (mg per cc)	0.50
Ascorbic Acid	8.16
Calcium Pantothenate	2.04
Nicotinic Acid	0.88
Pyridoxine Hydrochloride	2.73
Riboflavin	<0.006
Thiamine Hydrochloride	5.14
Vitamin A (12% in oil)	insol.
Organic Substances	
Acacia Gum	<0.16
Calcium Glycerosphosphate	<0.07
Cetyle Alcohol	0.23
Pectin	insol.
Phenothiazine (Purified)	<1.15
Sodium Citrate	0.23
Tannic Acid	>45.20
Inorganic Substances	
Arsenious Acid	insol.
Cupric Oxide	insol.
Ferric Oxide	insol.

*Viscosity of solutions prevented further additions of solid.

> = greater than.

insol. = not soluble.

∞ = miscible or soluble in all proportions.

< = less than.

Safe Handling And Storage

The storage and handling of propylene glycol presents no unusual problems, since this material has a pour point of less than –71°F (–57°C), is noncorrosive, has a flash point of 220°F (104°C) and poses no significant hazard to human or animal health or the environment.

The preferred material of construction for storing propylene glycol is stainless steel; however, epoxy or phenolic resin linings in carbon steel are acceptable. Unlined carbon steel tanks are a source of color and iron contamination and should be avoided to maintain the quality of the propylene glycol.

Propylene glycol will deteriorate slightly in air at ordinary temperatures (this effect is noticed principally in the odor and taste); consequently, an inert gas, preferably dry nitrogen, should be used in the vapor space of the tank to eliminate oxygen. Since propylene glycol is very hydroscopic, the use of dry nitrogen will also prevent the accumulation of water in the tank.

For ease of pumping it is recommended that propylene glycol be stored above 35°F (2°C). If internal heating coils or external electrical heaters are used to maintain pumpability, caution should be taken to ensure that the glycol is not being subjected to high metal surface temperatures (above 275°F [135°C]). Maximum suggested steam pressure is desuperheated 30 PSIG.

The recommended shelf life for bulk or factory packed drums of propylene glycol is twelve months under normal warehouse or bulk storage tank conditions. The quality of stored propylene glycol can be checked by monitoring acidity, color and odor. Good Manufacturing Practices must be followed to maintain USP status.

Additional information to assist in designing a bulk storage tank for propylene glycol is available in the Dow publication, *A Guide To Glycols*.

FOR
CHEMICAL EMERGENCY
(Spill, Leak, Fire, Exposure or Accident)

In the U.S., Call:
CHEMTREC
1-800-424-9300

In Canada, Call:
CANUTEC
1-613-996-6666

HAZARDS AND FIRST AID

Propylene glycol is very low in single dose acute oral toxicity. The single dose LD50 for laboratory rats ranges from 19,800 to 33,700 mg/kg. Chronic oral toxicity is also very low. Studies have shown that rats are unaffected when fed 10% propylene glycol in drinking water for 140 days. Because of its low chronic oral toxicity, propylene glycol is generally recognized as safe (GRAS) by the U.S. FDA for use in foods and pharmaceuticals when manufactured and used in accordance with U.S. FDA requirements. Historical data demonstrates that humans, like animals, are unaffected by low dosages of propylene glycol.

Prolonged contact is essentially nonirritating to skin. Repeated exposure may cause flaking and softening of skin. A single prolonged exposure is not likely to result in the material being absorbed through skin in harmful amounts. It may be absorbed in potentially harmful amounts when applied in large quantities to severe burns (second or third degree) over large areas of the body as part of a cream or other topical application.

At room temperatures, inhalation of propylene glycol vapors is not likely because of its very low vapor pressure. Exposure to mists or artificial fogs may be irritating to the upper respiratory tract and should be avoided. Although the U.S. EPA has established no required exposure guideline for propylene glycol in the workplace, the American Industrial Hygiene Association recommends a maximum eight-hour-time-weighted average for total vapor and aerosol of 50 ppm.

Regulatory Status

Propylene Glycol USP meets the requirements of the Food Chemicals Codex and can, therefore, be used for direct as well as indirect food additive applications. Food grade propylene glycol is considered to be generally recognized as safe (GRAS) as a multiple purpose food substance under U.S. 21 CFR 184.1666. Because of this GRAS status, Propylene Glycol USP may be used for indirect food applications which allow additives generally recognized as safe. In addition, a number of standardized foods allow for the use of optional ingredients which are "safe and suitable." Propylene Glycol USP will qualify where the use is suitable. These standardized foods are described in sections 133.128 (cottage cheese), 133.131 (low fat cottage cheese), 135.110 (ice cream and frozen custard), 135.120 (ice milk), 135.130 (mellorine), 135.140 (sherbets), 135.160 (water ices), 169.175 (vanilla extract), 169.176 (concentrated vanilla extract), 169.177 (vanilla flavoring), 169.178 (concentrated vanilla flavoring), 169.180 (vanilla-vanillan extract) and 169.181 (vanilla-vanillan flavoring). Propylene Glycol USP is also generally recognized as safe in animal feeds as a general purpose food additive (582.1666) and as an emulsifying agent (582.4666). The regulations should be consulted for full details.

The antimicrobial properties of propylene glycol have been reported numerous times.[9,10] Since antimicrobials may be regulated as pesticides, obtain guidance from the appropriate governing agencies (such as the Environmental Protection Agency [EPA] in the U.S.) before commercializing any product containing propylene glycol as an active pesticidal ingredient. In regard to use as an animal feed preservative, it should be noted that in 1993 Dow discontinued registration of SIRLENE* food grade propylene glycol under the U.S. Federal Insecticide, Fungicide, Rodenticide Act (FIFRA).

Dow And Product Stewardship

Concern for the proper handling and use of Dow Propylene Glycol USP is not something Dow surrenders at the customer's gate. The product stewardship philosophy of The Dow Chemical Company states that Dow has "a fundamental concern for all who make, distribute and use (our) products, and for the environment in which we live." To that end, The Dow Chemical Company subscribes to Responsible Care® codes that were created to inform our customers on how to operate more safely, remain responsible to government regulations and minimize the liability associated with the products purchased. Dow encourages its customers to review their applications for Dow products from the standpoint of human health and environmental concern and to help ensure that Dow products are not used in ways other than as intended or tested.

Technical Service and Development (TS&D) assistance for Dow customers on stewardship matters is available, together with materials on the proper handling of propylene glycol. Material Safety Data Sheets are also available.

Responsible Care®

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® Service Mark of The Chemical Manufacturers Association

PROPERTIES

Formula	CH_3-CHOH-CH_2OH
Molecular Weight	76.1
Boiling Point, 760 mm Hg	369.3°F (187.4°C)
Freezing Point	Supercools
Specific Gravity	
68/68°F (20/20°C)	1.038
77/39°F (25/4°C)	1.033
140/39°F (60/4°C)	1.007
Pounds per Gallon, 77°F (25°C)	8.62
Refractive Index, 77°F (25°C)	1.431
Viscosity Centipoise	
77°F (25°C)	48.6
140°F (60°C)	8.42
Specific Heat, cal/gm/°C, 77°F (25°C)	0.60
Vapor Pressure, mm Hg, 77°F (25°C)	0.13
Surface Tension, dynes/cm., 77°F (25°C)	36
Flash Point, Seta Flash	220°F (104°C)

These properties are laboratory results typical of the product, and should not be confused with specifications as shown below.

SPECIFICATIONS

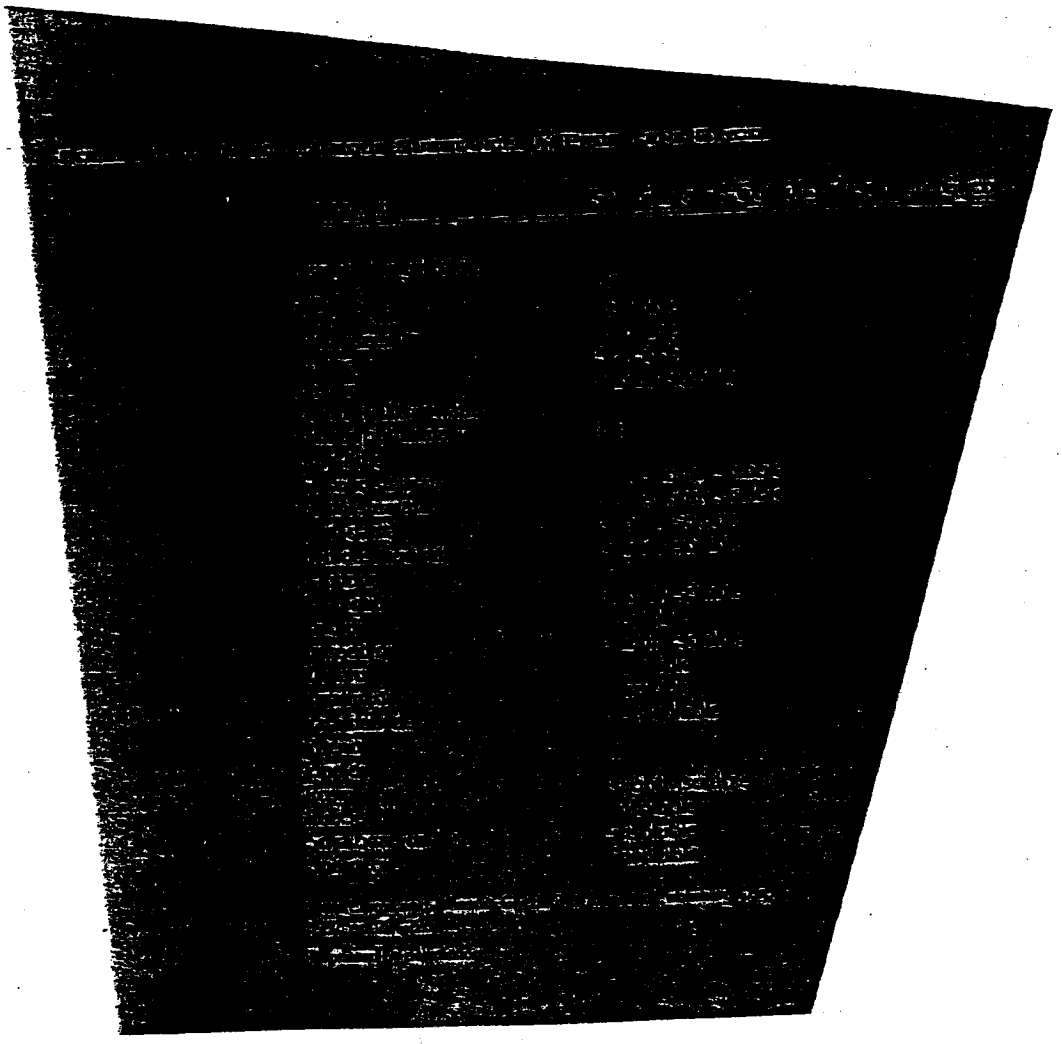
*Specific Gravity, 68/68°F (20/20°C)	1.0376-1.0389
*Specific Gravity, 77/77°F (25/25°C)	1.0352-1.0364
*Distillation Range, 760 mm Hg, IBP-DP	367-372°F (186-189°C)
Acidity (as acetic acid), Maximum	20 ppm
Chlorides, Maximum	1 ppm
Sulfates	Conforms
Heavy Metals (as Pb), Maximum	5 ppm
Arsenic (as As_2O_3), Maximum	1 ppm
Iron, Maximum	0.3 ppm
Solubility, 77°F (25°C)	Miscible in all proportions with water, acetone and chloroform
Assay (as $C_3H_8O_2$), by Weight, Minimum	99.5%
Water, Maximum	0.2%
Ash (sulfated), Maximum	0.005%
APHA color, Maximum	10
Odor	Practically odorless
Taste	Slight characteristic
Suspended Matter	Substantially free
Organic Volatile Impurities	Conforms
Residual Propylene Oxide, Maximum	5 ppm

All values by U.S.P. XXII methods of analysis

*Not a specification requirement.

TABLE 5

PHYSICAL PROPERTIES DATA



FOOTNOTES

1 U.S. Patent 4,600,586. "Livestock Feed Lot Adaptation Composition and Method," July 15, 1986.

2 "Detection, Occurrence, and Prophylactic Treatment of Borderline Ketosis with Propylene Glycol Feeding," *Journal of Dairy Science*, Vol XLVII, No. 10, pp. 1074-1079, October, 1964.

3 "Final Report on Safety Assessment of Propylene Glycol," Expert Panel of *Cosmetic Ingredient Review*, The Cosmetic Ingredient Review, The Cosmetic, Toiletry, and Fragrance Association, Washington, DC, 1993.

4 Ernest W. Flick, *Cosmetic and Toiletry Formulations*, Second Edition, Noyes Publications, 1989.

5 D. F. Williams, W.H. Schmitt, *Chemistry and Technology of the Cosmetics and Toiletries Industry*, Blackie Academic & Professional, New York, 1992.

6 EP 404,533, Procter and Gamble Co. (Dec. 1990).

7 JP 01,238,521, Lion Corp. Ajinomoto Co. Inc. (Sept. 1989).

8 JP 02,264,712, Nisshin Oil Mills Ltd. (Oct. 1990).

9 "A Study of the Inhibitory Concentrations of Glycenn-Sorbitol and Propylene Glycol-Sorbitol Combinations on the Growth of Microorganisms," *Journal of American Pharmaceutical Association*, Vol XLVI, No. 4, p. 217-218.

10 "Activity of Propylene Glycol on Bacteria: Influence on Growth Rate in a Liquid Medium," *Arch. Hyg. Bakteriol* 147, p. 189-200, 1963.

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