

Alfred Bader fonds

Correspondence

Hinshaw + Culbertson  
(AB consulting - lawsuit)  
1995

QUEEN'S UNIVERSITY ARCHIVES	
LOCATOR	5095.5
BOX	5
FILE	22







November 7, 1995

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

Please don't mind that I am responding to your letter of September 22nd only today, but you sent it to Bexhill-on-Sea, from where it was forwarded to us here in Milwaukee. We will be in Bexhill from November 13th through December 24th, but until next Monday, we are in Milwaukee.

As I had not heard from you in response to my letter of August 17th and the invoice enclosed therewith, I feared that you might somehow not be satisfied with the help I tried to give. But perhaps my letter and invoice got lost in the mails, and so I enclose copies.

By now, you might have finished reading my book. If you have read chapters 7, 12 and 13, you will realize how the culture at Aldrich and Sigma-Aldrich has changed over the years. I always tried to help all chemists, whether customers, suppliers or competitors, but that unfortunately is no longer so.

Aldrich would not allow Bob Langa to consult for Tokyo Kazai, and I am afraid that I do not know of experts elsewhere either in OSHA matters or with explosives.

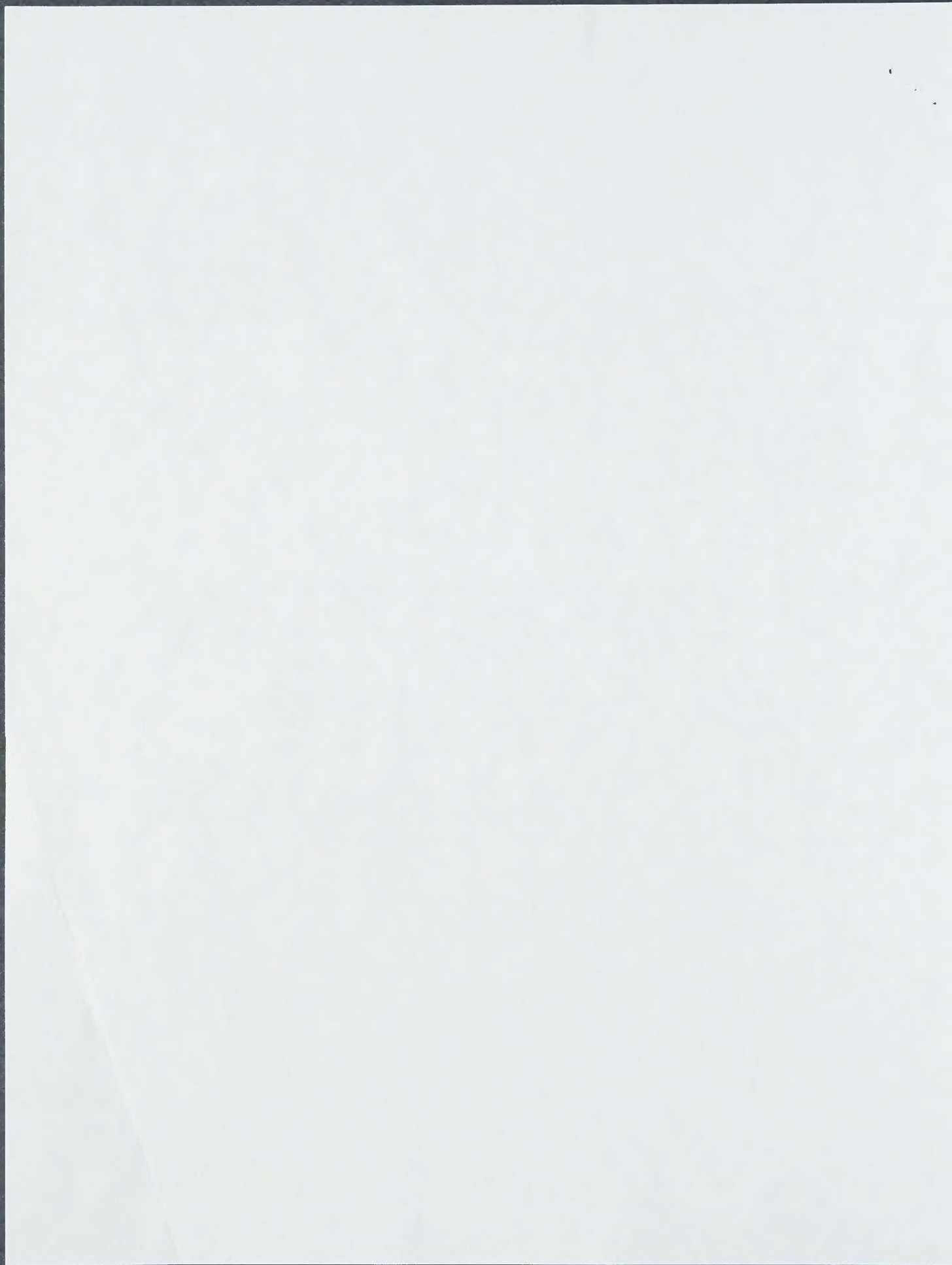
With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosures







August 17, 1995

**INVOICE**

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Your file no. 726608

For consultation re: the explosive nature of dimethyl azodicarboxylate,  
circa 5 hours at \$100.00/hour

**NET DUE: \$500.00**

NB: For your records, my Social Security number is [REDACTED].



1975-76

1976-77

1977-78  
1978-79  
1979-80  
1980-81

1981-82  
1982-83

1983-84

1984-85



February 22, 1996

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

As you will be able to imagine, I have been trying to think of the right expert in the field of explosives but have not been able to find such a person.

Regarding an expert in government regulations generally, one logical person is Dr. Ike Klundt, who retired from Aldrich some years ago after being a vice president in the company for many years. He is now partially retired, living in Colorado, and I understand from Tokyo Kasei that you are in touch with him. That is certainly a good decision.

I enclose a copy of my invoice for consulting, which must have been overlooked.

With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosure



1912-1913

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August 17, 1995

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

I really enjoyed meeting you today. I hope that my discussion and also yours with Bob Lenga were helpful to you.

I think the three most important points coming from our discussion are:

- 1) that there were at least three other hazardous chemicals thrown away at the same time, namely benzyl chloroformate, hydrazine hydrate and propiolic acid;
- 2) Dr. Jay Young included a serious mistranslation of the original German paper. There is a world of difference between a compound "going pop" and exploding; and
- 3) that the preparation of dimethyl azodicarboxylate is described in detail in a standard text, Organic Syntheses, which describes the preparations of many common and widely used reagents. Only in a warning dated June 1995 did Organic Syntheses point out that dimethyl azodicarboxylate can explode on heating.

We agreed that I would bill you \$100.00 per hour for consulting, but only for solid hours of work. I hope that you will call me or fax me from time to time to tell me about developments, and of course, a few minutes' involvement on the phone or in my library will not be charged.

With all good wishes, I remain,

Yours sincerely,

AB/cw  
Enclosure - Invoice



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ETHYL CARBONATE

CH<sub>3</sub>CH<sub>2</sub>OC(=O)CH<sub>2</sub>CH<sub>3</sub>

H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O  
C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>CN<sub>2</sub>·H<sub>2</sub>O  
C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>CN<sub>2</sub>·H<sub>2</sub>O

A. Ethyl carbamate. A 250-ml. flask equipped with a magnetic stirrer, reflux condenser, and a thermometer (100°C. scale) is charged with 100 g. (3 moles) of 10% aqueous ammonia (33.3 g. of ammonia hydrate) in 70 ml. of water. The flask is placed in an ice bath and the stirring is continued. 100 g. (3 moles) of ethyl cyanate (326 g. (3 moles) of ethyl isocyanate) is added with stirring at a rate which maintains the temperature between 15° and 20°. The reaction mixture has been introduced in a series of 40-g. (1.5 mole) portions of sodium carbonate in 100-ml. portions. The reaction continues with the remaining sodium carbonate. The addition of the two reactants is continued until the temperature rises above 20°. The reaction is complete slightly before the addition of the last portion of sodium carbonate, maintaining an excess of 10% of cyanate in the mixture at all times. During the course of the reaction, the mixture is kept stirred.

After addition of the last portion of sodium carbonate, the flask are washed with water. The reaction mixture is then collected in a 250-ml. flask and a total of 100 ml. of cold water is added. The mixture is then stirred and maintained 215-220°C. for 1 hour.







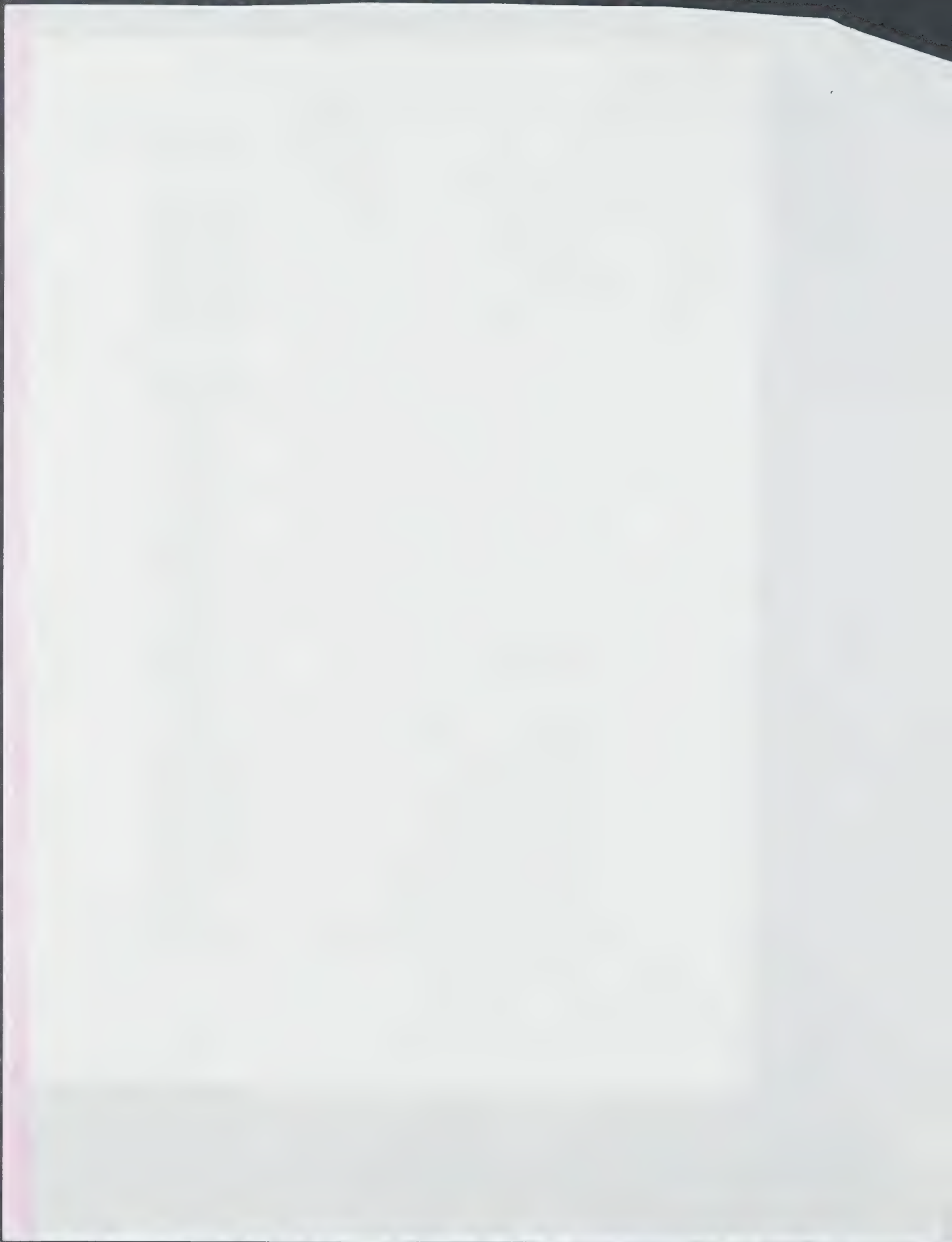
melts at 131–133°. It is sufficiently pure for the preparation of ethyl azodicarbonyl diethylcarbamate.

*R. Litt, J. Org. Chem., 19, 407 (1954). Ethyl and methyl azodicarbonyl diethylcarbamate is prepared in a sealed capillary tube which is protected from air. Overheating is to be avoided and the reaction is carried out in an electrically heated mantle. The reaction is carried out in a sealed tube. Since copious fumes of nitrogen gas are evolved, the reaction by nitric acid distillation and the separation of the product should be carried out in a well-ventilated area.*

A mixture of 200 g. (1.0 mole) of diethylamine in 125 ml. of 70% nitric acid is placed in a 250-ml. flask equipped with a mechanical stirrer, a thermometer, and a thermometer. The reaction is carried out at a temperature of 93–95° in a fuming nitric acid (95–100% HNO<sub>3</sub>) atmosphere. The reaction mixture is stirred and is then cooled by pouring it into 500 g. of ice, 500 ml. of water, and 100 ml. of concentrated sulfuric acid in a 2-l. beaker cooled in a bath of crushed ice. The solution is stirred and the organic layer is separated. The organic

layer is washed with 100 ml. of water. The organic layer is washed with 100 ml. of water and dried with anhydrous magnesium sulfate (Note 5) with three 10-ml. portions of water. The combined organic layers are washed with 500 ml. portions of ice water and are then stirred for 10 minutes with 500 ml. of ice water. The organic layer is finally washed with 100 ml. of ice water and dried quickly with a small portion of anhydrous magnesium sulfate that is removed by filtration. The solution is dried overnight with a fresh portion of anhydrous magnesium sulfate. *Caution! The following distillations should be well shielded.* The methylene chloride is removed by washing with 100 ml. of water. The residue is rapidly distilled with an 8-mm. fractionating column (1–5 mm.) from a flask immersed in an ice-water bath. The temperature is raised gradually to 115–118°. The residue is then fractionally distilled on a 10-ft. fractionating column packed with glass beads, using a 100-ml. distillation flask. The product is collected at 93–95°/5







mm. There is obtained 135-158 g. (70-80%) of ethyl azodicarboxylate which freezes at 67° (Notes 6, 7, and 8).

#### Notes

1. The thermometer and one of the funnels are fitted to a two-necked adapter so that, when the thermometer bulb is immersed in the solution, the range between 10° and 20° is easily visible.

2. Ethyl hydrazodicarboxylate may be purified by crystallization from diethyl ether, m.p. 134°.

3. Methyl hydrazodicarboxylate, which is much more soluble in water than the ethyl ester, may be prepared by the following modification of the above procedure.

A solution of 100 g. (2 moles) of hydrazine hydrate in 800 ml. of 95% alcohol is treated as described above with a total of 378 g. (4 moles) of methyl chloroformate while maintaining the temperature below 20°. During the addition of the last half of the chloroformate, a warm (50-55°) solution of 212 g. (2 moles) of sodium carbonate in 800 ml. of water is added. The resulting slurry is stirred for 30 minutes, and the precipitate is filtered on a Büchner funnel, washed with 100 ml. of ice water, and air-dried. The nitrate is concentrated at reduced pressure (12-25 mm.) on a water bath to 700 ml. and is cooled in ice. The precipitate is filtered, washed with 100 ml. of ice water, and air-dried. The combined crops of crude methyl hydrazodicarboxylate are dried at 60° in a vacuum oven and are then stirred successively with two 600 ml. portions of warm acetone to separate inorganic impurities. The acetone solution is filtered, and evaporated at reduced pressure to yield 260 g. (88%) of methyl hydrazodicarboxylate (m.p. 127-131°) of sufficient purity for preparation of methyl azide.

A purer product (m.p. 131-132°) may be obtained by washing the acetone solution with 500 ml. and adding to it 1.8 l. of heptane. Heptane also was used to 80%. The solution is cooled and allowed to settle.

4. As a safety precaution, in case the beaker should break, it is placed in a 1-gal. can.

5. The separatory funnel should be vented frequently at frequent intervals since large quantities of nitrogen evolve.







6. The same after... can be  
... somewhat  
... analysis than

A solution of 20 g of 25% ... hydrazodicar-







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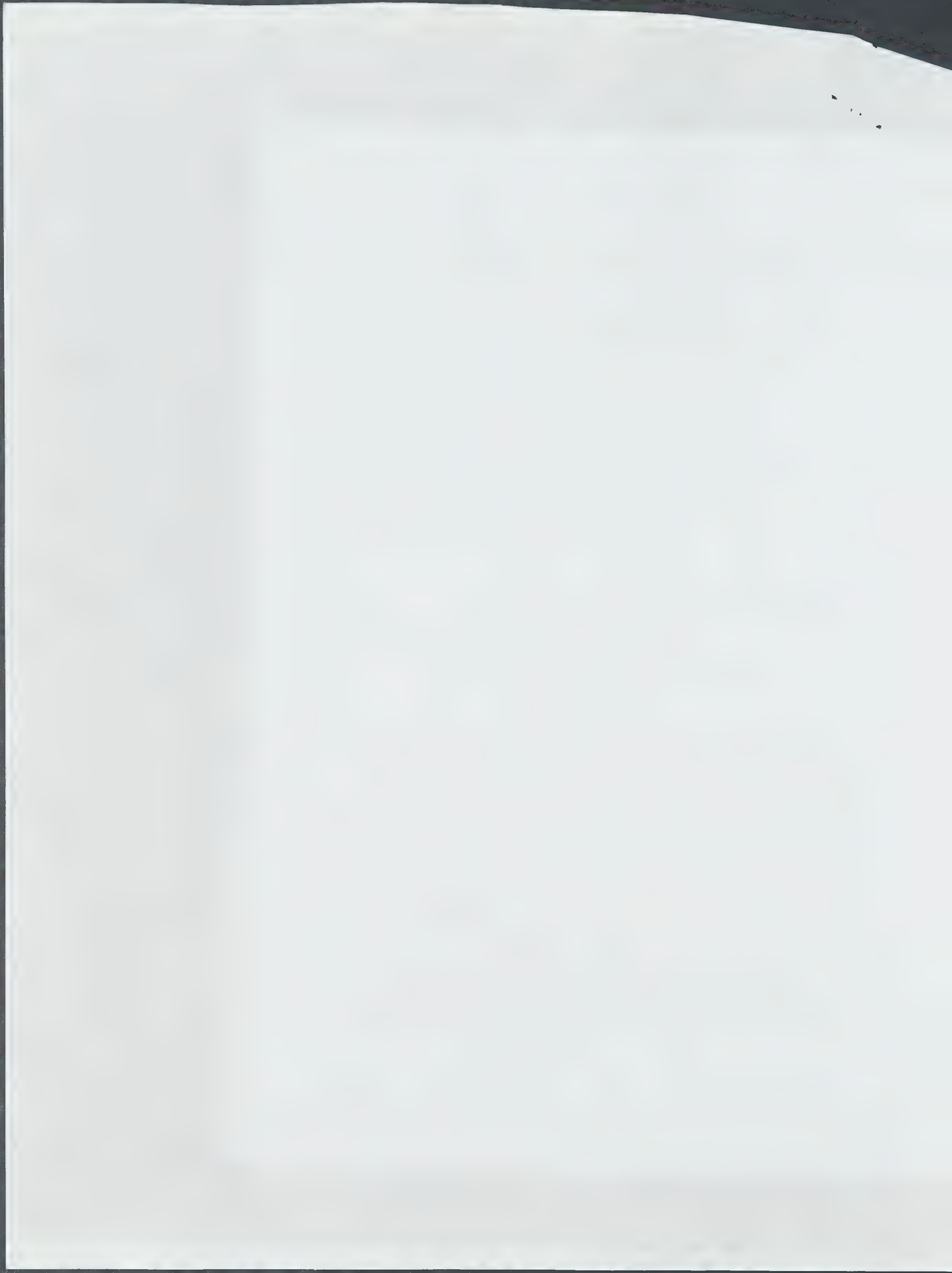
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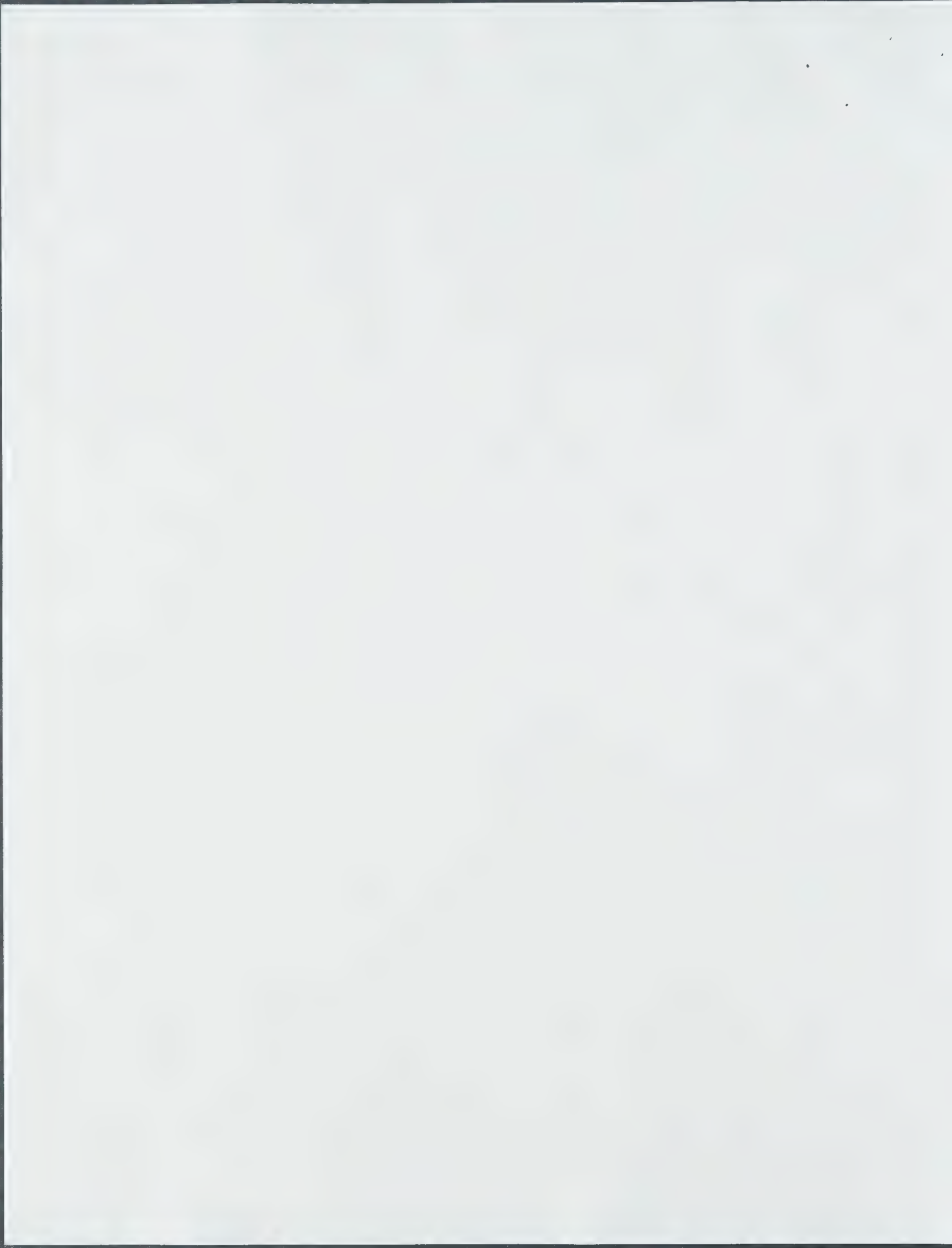
SENT BY:LANDAU OMAHANA & KOPKA; 4-24-95 ; 17:47 ;

LOK→

815 987 4092;#15/25

**ATTACHMENT A1**





CONTAINER CONTENTS

Bulk  Mixed Lab

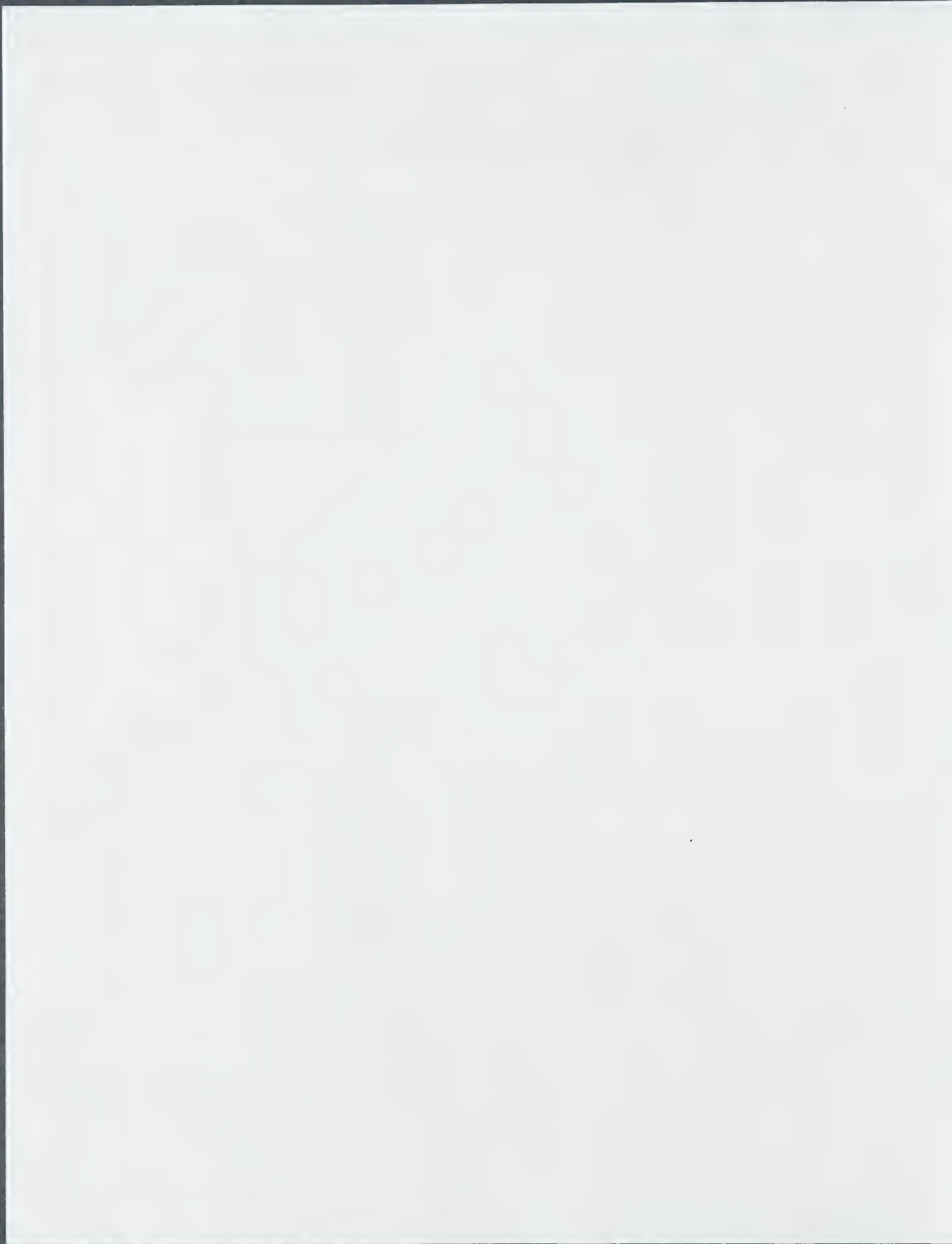
Receiving	Routing	Shipping
LRC- Acid LIQ		OR

Container Number: 940830-6DS-31  
 DOT Shipping Name: Waste Corrosive Liquids  
 Container Type: 7H 30  
 Hazard Class: 8 (6.1) I

Line No	Material Description	Material Quantity	RQ	EPA Waste Code Number
1	Benzyl Chloroformate III I	3 x 1pt		D002
2	Hydrazine Hydrate	1 x 1pt + 1#	RX	D003
3	Ammonium Sulfide	1 x 1/2 x 3#	RX	D003
4	Titanous Chloride Soln.	1 x 1pt	RX	I
5	Acetic Anhydride	1 x 5ml	RX	I
6	Phosphoric Acid	1 x 1gal		
7	Hydrochloric Acid	I		
8	Gluconic Acid	1 x 1L		
9	Nonanoic Acid	I		
10	Gluconic Acid II	2 x 1L		
11	Trifluoroacetic Acid	1 x 1pt		
12	Hydrazine Monohydrate II	2 x 1pt		
13	Hydrobromic Acid	1 x 1pt		
14	Hydroiodic Acid III	4 x 1pt		
15	Glyoxylic Acid	1 x 1pt		
16	Formic Acid III	3 x 1pt		
17	Isobutyric Acid	1 x 1L		
18	Fumaryl Chloride	1 x 100ml		
19	Crotonic Acid II	2 x 50ml		
20	2-Bromo-4-nitroacetophenone	1 x 75ml		
21	Thioacetic Acid (Stench)	2 x 100ml	RX	D003
22	Propionic Acid II	2 x 100ml		
23	Cyclohexanecarboxylic Acid III	3 x 100ml		
24	3-Bromobenzoyl Chloride	1 x 100ml		
25	Cyclopentanecarboxylic Acid II	3 x 100ml		
26	4-(3-aminopropyl) morpholine	1 x 100ml		
27	Methane Sulfonic Acid	I		
28	Chlorodifluoroacetic Acid II	2 x 100ml		
29	Valeric Acid II	I		
30	Propiolic Acid	1 x 100ml		

This Lab Pack list continues: Yes  No  This is page 1 of 2







# Container Contents

ARF No. \_\_\_\_\_

Bulk

Mixed Lab

Container Number: <u>9409330pc6DS-31</u>		Chemical: <u>DS</u>
DOT Shipping Name: _____		596 597
Container Type: _____	UN/NA Number: _____	HM _____
Hazard Class: _____		

Receiving	Routing	Shipping
		<u>LFC - Acid Lab OK</u>

Line No.	Material Description	Material Quantity	RQ	EPA Waste Code Number
01	Nitric Acid > 70% I	1x lot		D002
02	Bromoacetyl Bromide	1x 100ml		
03	Propionic Acid	I		
04	Bromobutyric Acid	1x 50ml		
05	4-Pentenoic Acid	I		
06	Valeric Acid	I		
07	Cyclopentyl Acetic Acid "	2x 50ml		
08	Cyclopropyl Carboxylic Acid "	I		
09	Chloromethanesulphonyl Chloride	1x 50ml		
10	Nonenoic Acid	I		
11	Azodicarboxylic Acid	I		
12	Dimethyl Ester	I		
13	Hydrochloric Acid	I		
14	Cyclopentane carboxylic Acid	2x 50ml		
15				
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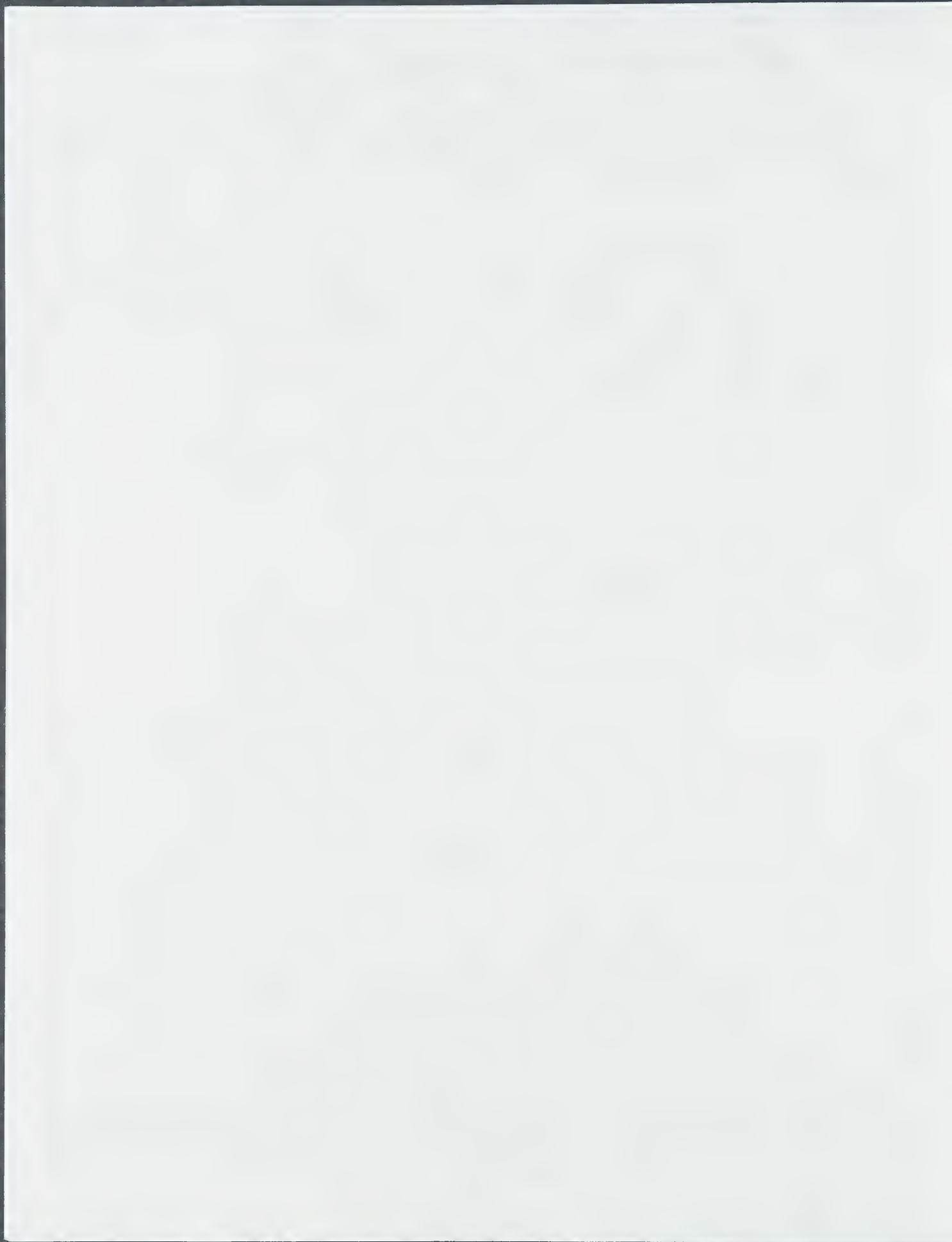
TRW = 6th

This Lab Pack list continues;

Yes  No

This is page 2 of 2





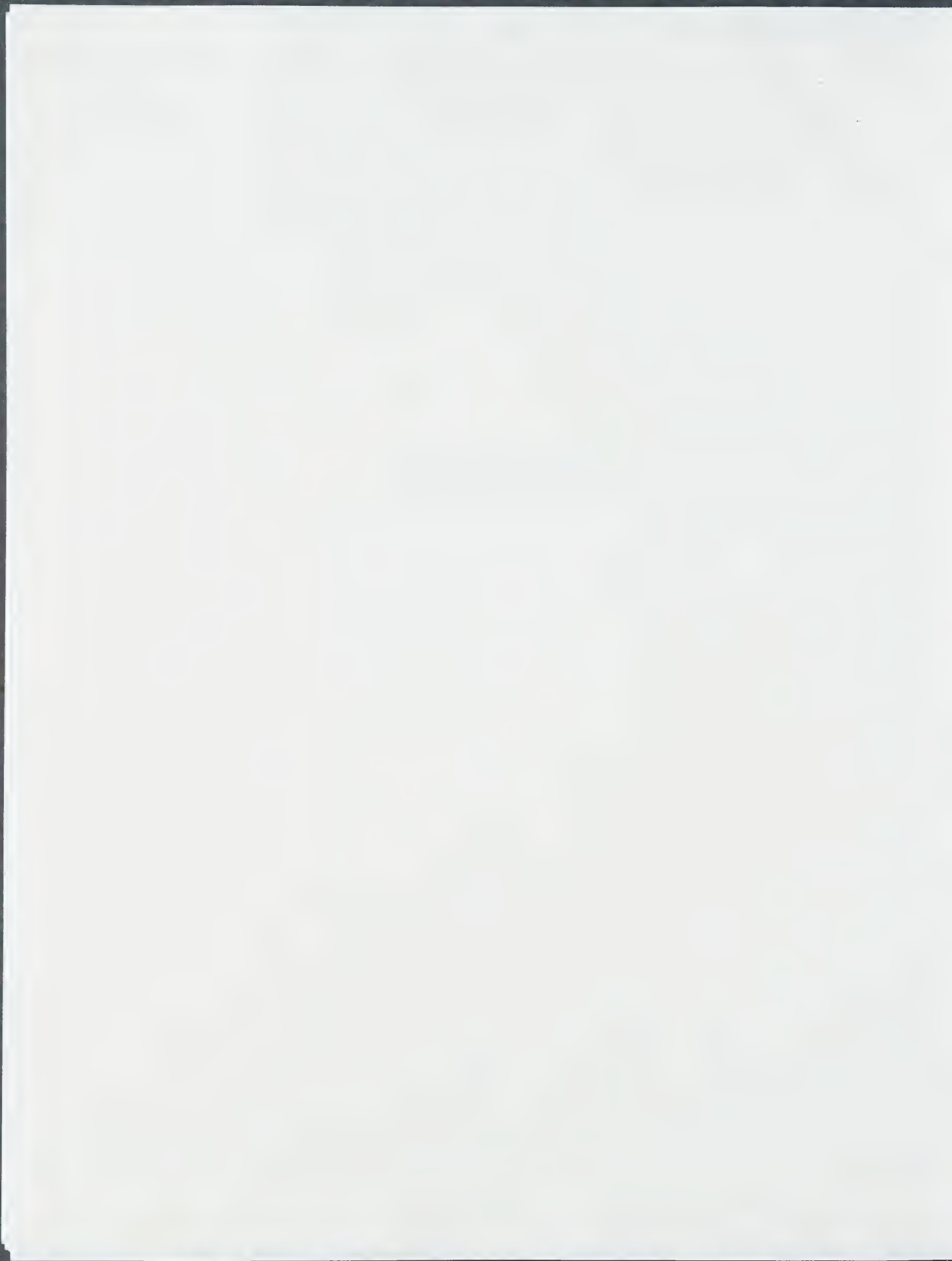
SENT BY: LANDAU OMAHANA & KOPKA; 4-24-95 ; 17:49 ;

LOK→

815 987 4092;#18/25

**ATTACHMENT A2**







# Container Contents

ARF No. \_\_\_\_\_

Bulk  Mixed Lab

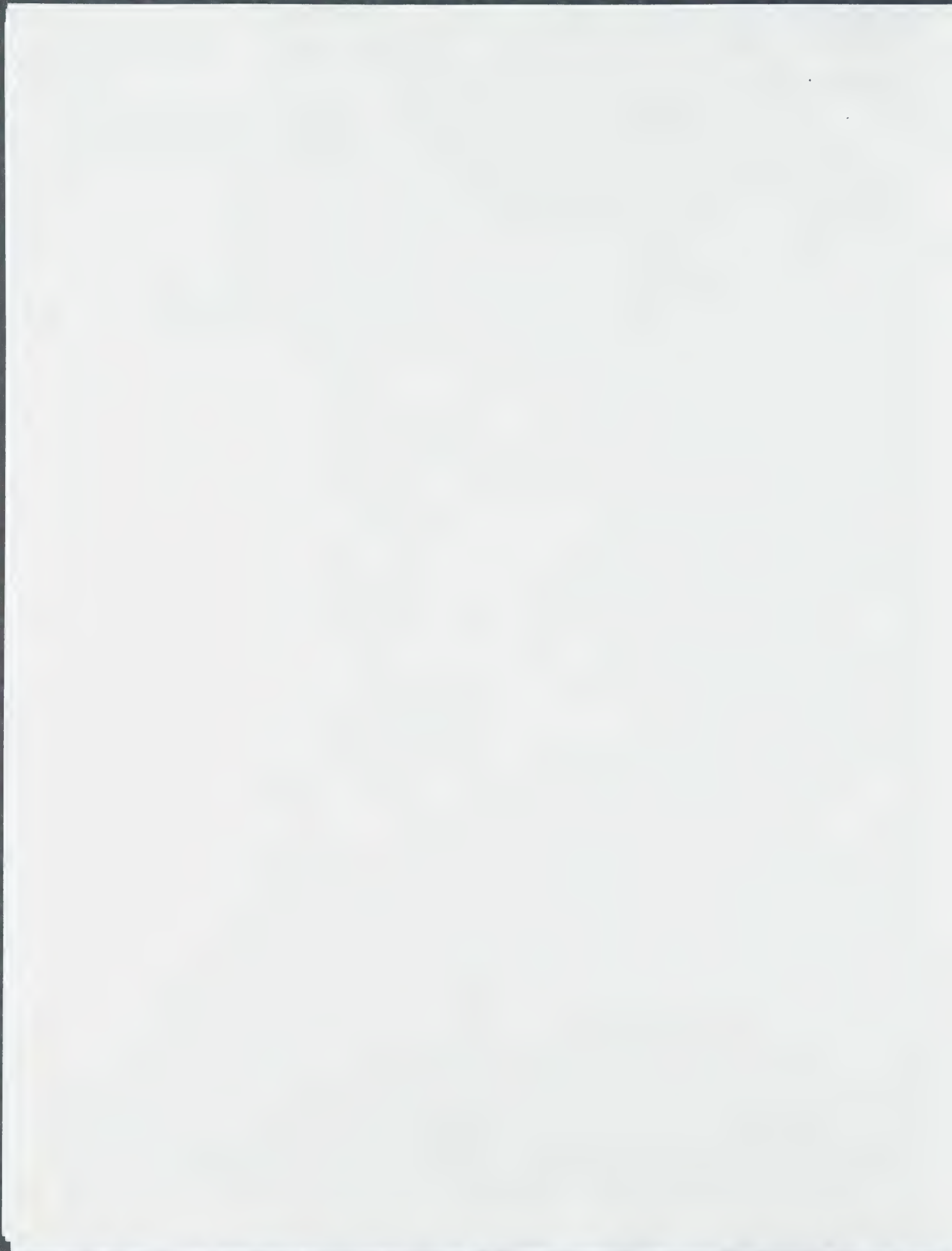
Container Number	040915pc WKC -- 70		Chemist
DOT Shipping Name	Waste Corrosive liquids N.D.S.		596 597
Container Type	UN/NA Number	HM	
Hazard Class	8		#

Receiving	Routing	Shipping

Line No.	Material Description	Material Quantity	RQ	EPA Waste Code Number
01	Phosphoric Acid II	x 1 qt		D002
02	Hydrochloric Acid III III III III III	x 1 gal		
03	" " I	x 1 qt		
04	Benzoic Acid	x 1 qt		
05	Sulfuric Acid I	x 1 qt		
06	Phosphoric Acid III III III	8 x 1 pt		
07	Acid	1 x 4 oz		
08	Phosphoric Acid	1 x 4 oz		
09	Trisodium Phosphate	1 x 1 pt		
10	Sulfuric Acid II	2 x 1 qt		
11	Hydrochloric Acid III III III	x 4 qt		
12	" " "	x 1 qt		
13	Ferric Chloride	1 x 1 pt		
14	Acidified Thiourea	1 x 1 pt		
15	Sulfuric Acid	7 x 1 qt		
16	Hydrochloric Acid	2 x 1 qt		
17	Stop bath w/ Acetic Acid	4 x 1 pt.		
18				
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This Lab Pack list continues; Yes  No  This is page 1 of 1





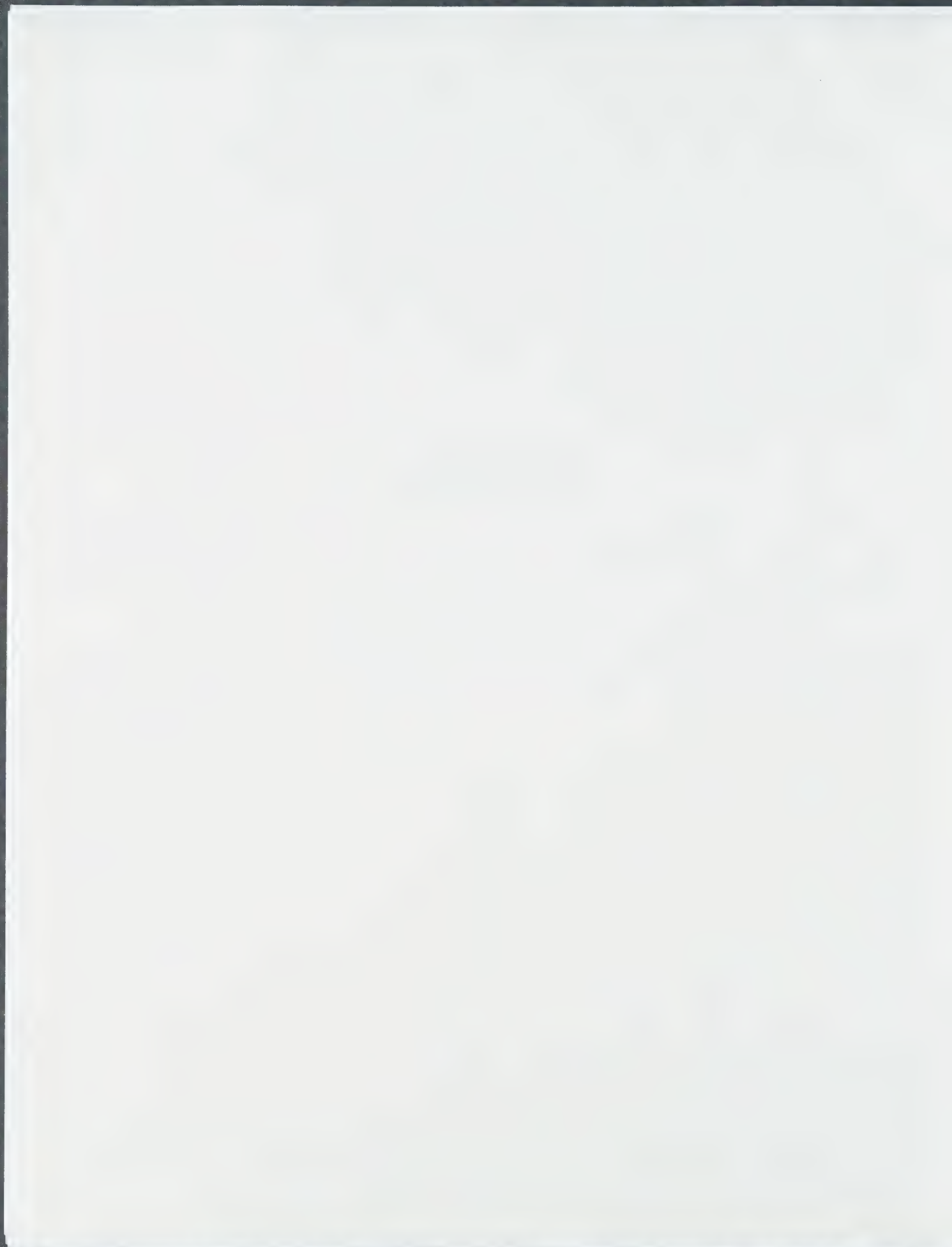
SENT BY: LANDAU OMAHANA & KOPRA, 4-24-95, 17:48 ;

LOK-

815 987 40921#20/25

**ATTACHMENT A3**





THIS WASTE DOES NOT CONTAIN ANY DIOXINS, CHLORINATED FURANS, EXPLOSIVES OR RADIOACTIVE MATERIALS.

TO9 - INCINERATION

# Container Contents

Bulk

Lab Pack

RQ \_\_\_\_\_

Container Number:	MONTH: 07	DAY: 06	YEAR: 94	CODE: LRBSP	NUMBER: 106	Chemist: CH
DOT Shipping Name:	Waste, Common Liquids, U.O.S.				Absorbent: (V)	
Container Type:	17H	Size: 55	UN/NA Number: UH1700	HM: <input checked="" type="checkbox"/>		
Hazard Class:	8 II					

Profile Number	
Disposal Site	Pec. -
Approval Code	
Reactive Wt.	

No	Material Description	PS	Material Quantity	I.C.	EPA Waste Code Number
01	Nitric Acid waste	L	(8 x 1/2) gal. ~ 40 #s	G	D002
02					
03	Sulfuric Acid waste	L	(1 x 1/2) gal. ~ 5 #s	G	D002
04					
05	Ammonium fluoride & Hydrochloric Acid	L	(1 x 1/2) gal. ~ 5 #s	P	D002
06					
07	Chromate	L	(1 x 1/2) gal. 28 #s	F	D002, D007
08					
09	Ammonium fluoride & Hydrochloric Acid	L	(2 x 1) gal. ~ 38 #s	P	D002
10					
11					
12	Formic Acid, spent	L	(2 x 1) gal. ~ 2 #s	G/P	D002
13					
14	Hydrochloric Acid	L	(1 x 1) gal = 1 #	G	D002
15	Phosphoric Acid	L	(3 x 1) gal. = 3 #s	G	D002
16					
17		L	(3 x 1/2) # = 1 1/2 #	G	D002
18					
19	Nickel Electroplate w/ Nickel Sulfamate	L	(5 x 1) gal. ~ 50 #s	P	D002
20					
21	Basic Acid & Sodium Large Sulfate, pH = 1.0	L	(2 x 1/2) gal. ~ 20 #s	P	D002
22					
23					
24					
25					
26					
27					
28					

ABSORBENT  
C - CORN COB  
V - VERMICULITE  
O - OTHER

PS - PHYSICAL STATE  
L - LIQUID / POURABLE  
S - SOLID  
X - SLUDGE

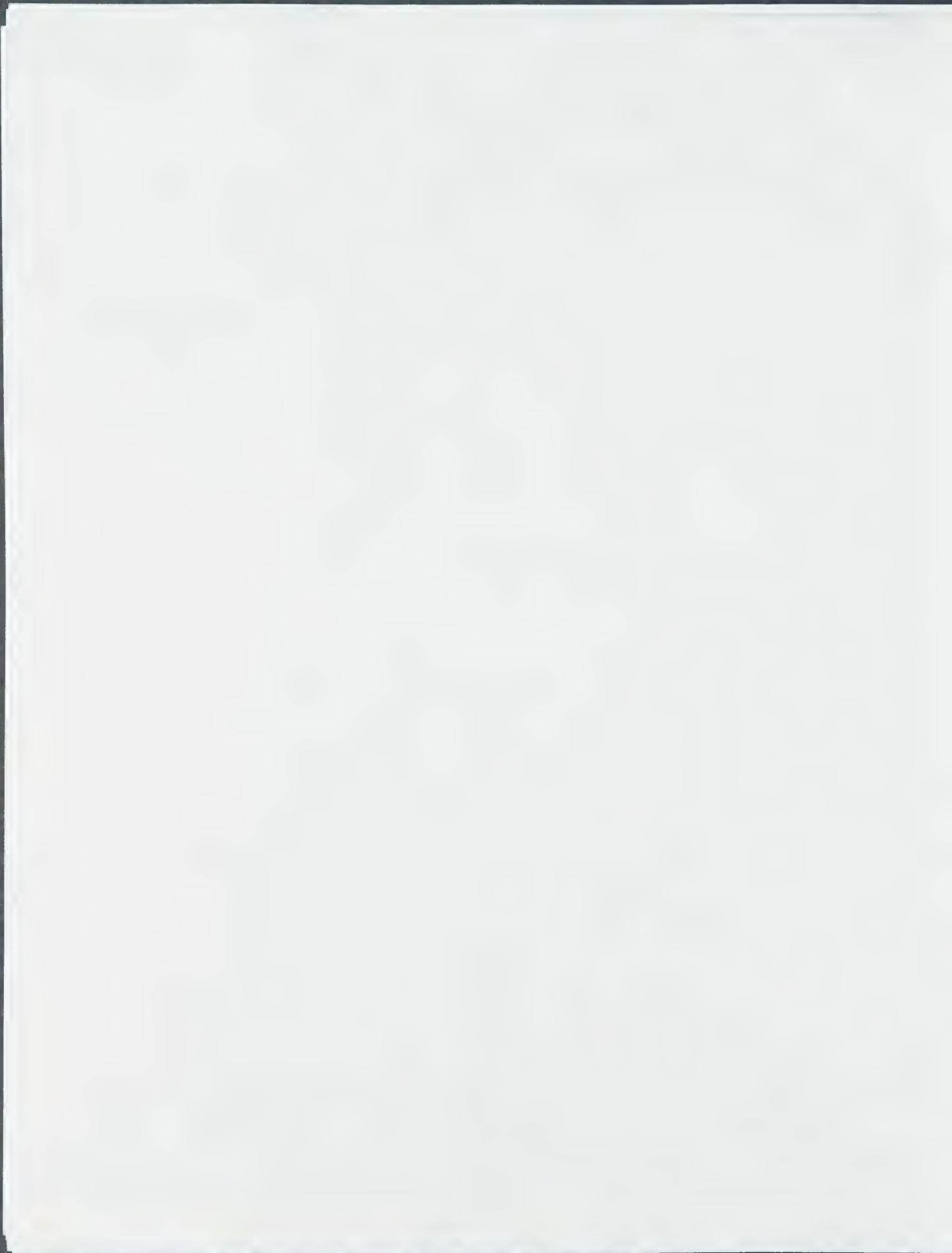
I.C. - INTERNAL CONTAINER  
G - GLASS M - METAL  
P - PLASTIC F - PAPER

This Lab Pack list continues: Yes  No

This is page 1 of 1

ORIGINAL - FINAL T.S.D. • GREEN TRANSPARENT • YELLOW-DISPOSER • PINK - 1ST T.S.D. • GOLD-GENERATOR





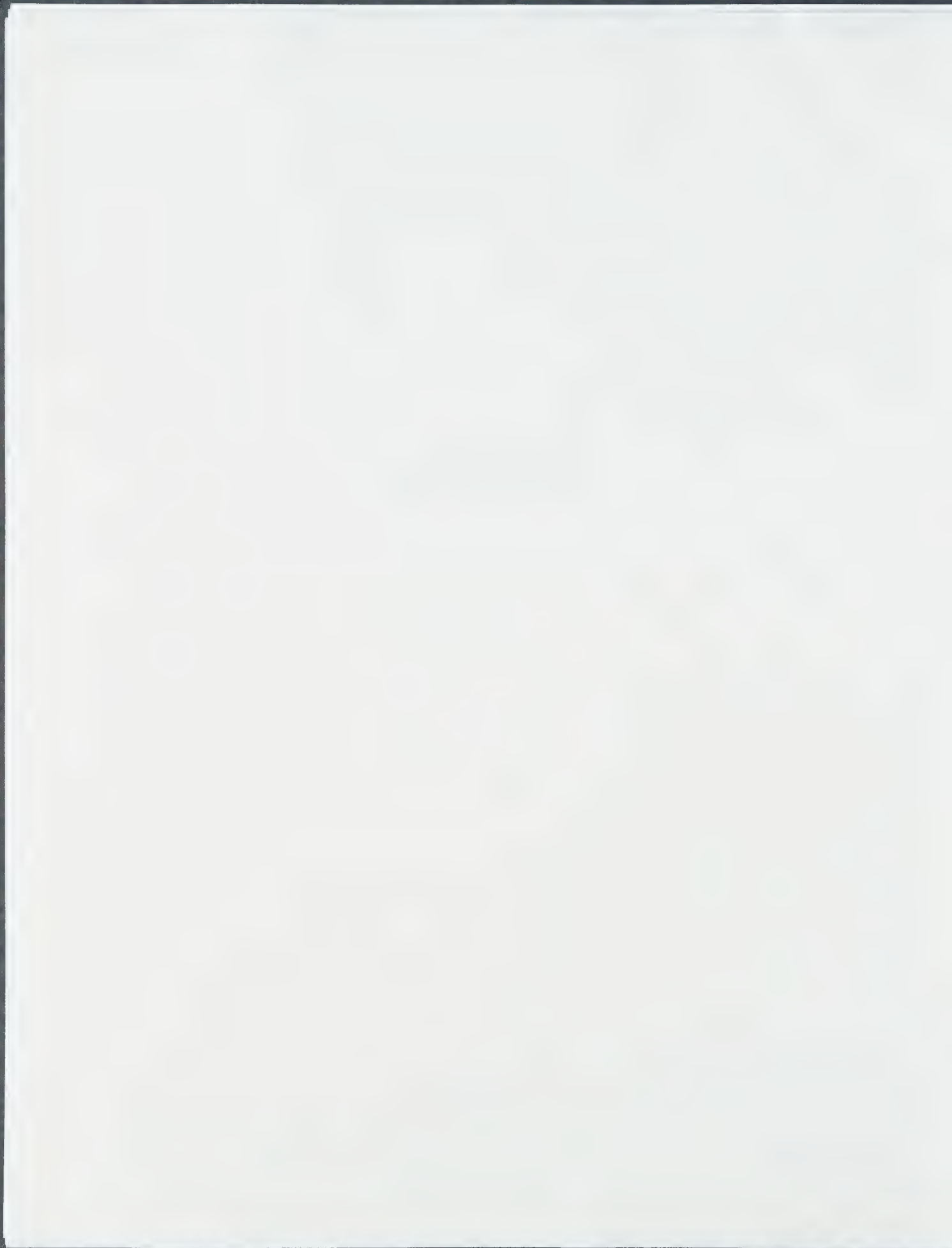
SENT BY:LANDAU OMAHANA & KOPKA; 4-24-95 ; 17:50 ;

LOK→

815 987 4092:#22/25

**ATTACHMENT A4**





THIS WASTE DOES NOT CONTAIN ANY DIOXINS, CHLORINATED FURANS, EXPLOSIVES OR RADIOACTIVE MATERIALS. T09 - INCINERATION

# Container Contents

Bulk

Lab Pack

RQ \_\_\_\_\_

Container Number:	MONTH: 09	DAY: 14	YEAR: 94	CODE: LRCH	NUMBER: 810	Chemist: PH
DOT Shipping Name:	LEASTE CORROSIVE LIQUIDS CO.					Absorbent: CVO
Container Type:	17H Size: 55	UN/NA Number: UN1765	HM: <input checked="" type="checkbox"/>			
Hazard Class:	8 PCTI					

Profile Number	
Disposal Site	PEC-UP
Approval Code	
Reactive Wt.	

Line No.	Material Description	PS	Material Quantity	IC	EPA Waste Code Number
01	Fiver w/	H	3 x 5gal		8102.D011
02	Silver and Acetic acid				
03					
04					
05					
06					
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28					

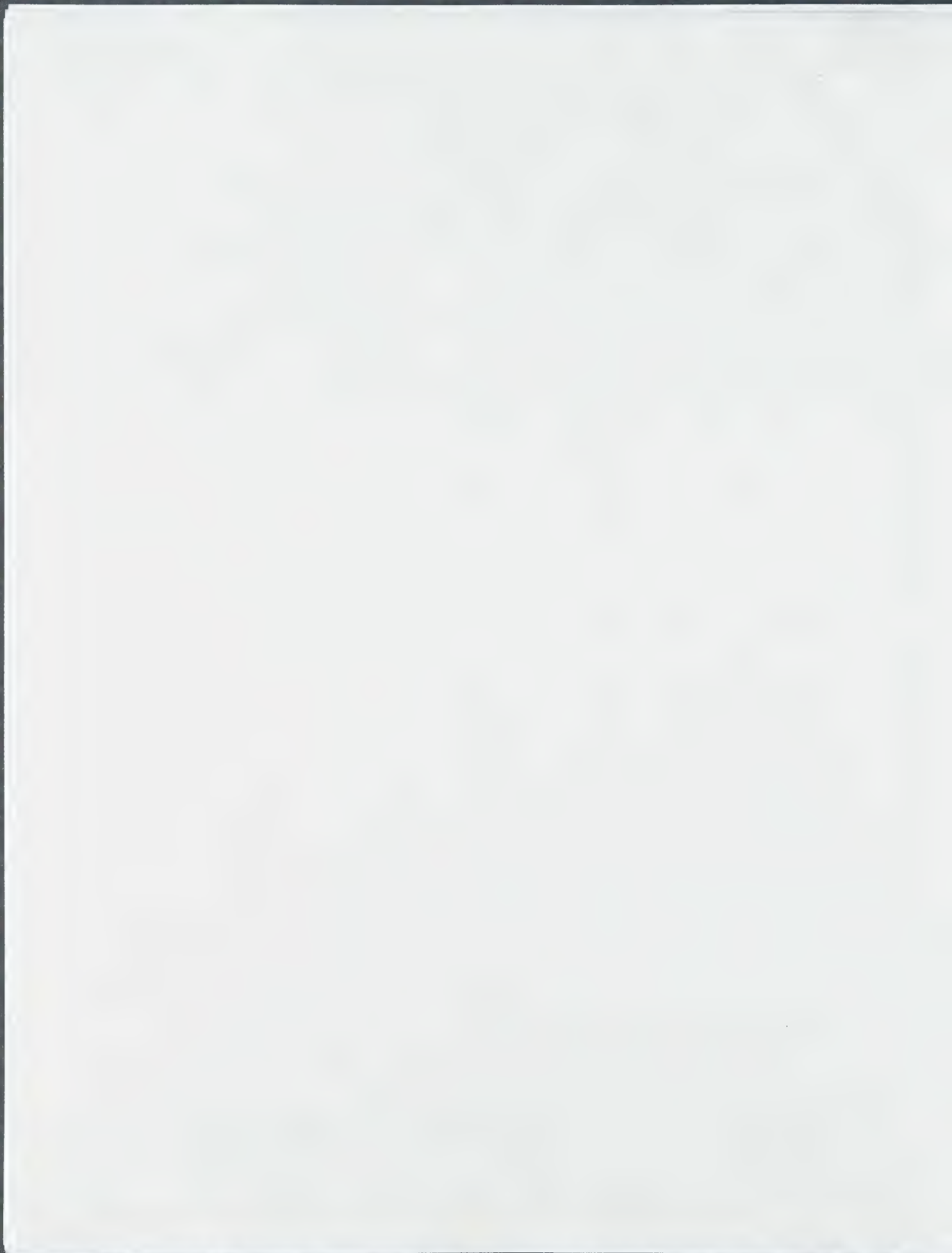
ABSORBENT  
 C - CORN COB  
 V - VERMICULITE  
 O - OTHER

PS - PHYSICAL STATE  
 L - LIQUID / POURABLE  
 S - SOLID  
 X - SLUDGE

IC - INTERNAL CONTAINER  
 G - GLASS M - METAL  
 P - PLASTIC F - PAPER

This Lab Pack list continues: Yes  No

This is page \_\_\_\_\_ of \_\_\_\_\_



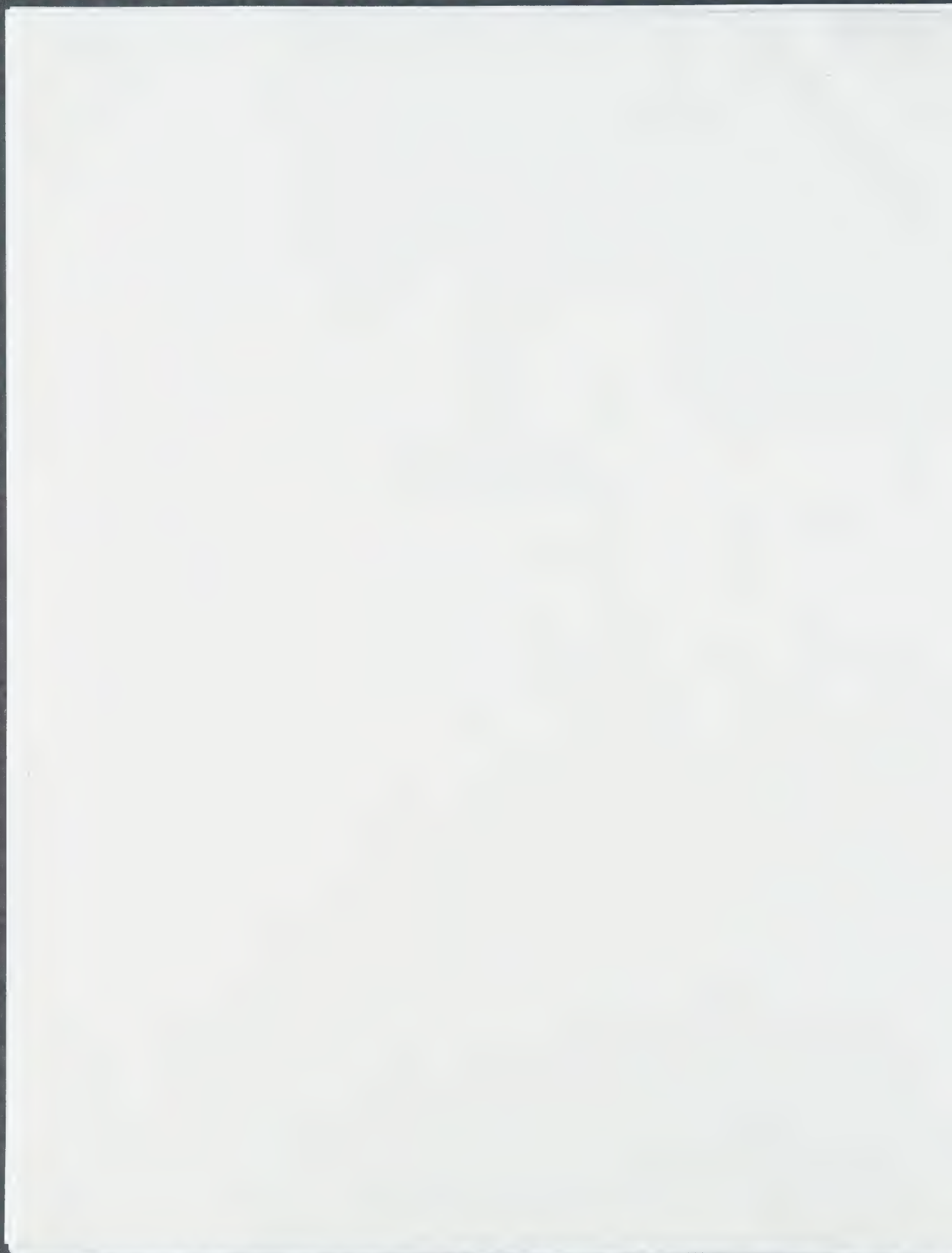


SENT BY: LANDAU OMAHANA & KOPKA; 4-24-95 ; 17:51 ;

LOK→

815 987 4092; #24/25

**ATTACHMENT A5**



SENT BY: LANDAU OMAHANA & KOPKA; 4-24-95 ; 17:51 ;

LOK-

815 987 4092; #25/25

THIS WASTE DOES NOT CONTAIN ANY DIOXINS, CHLORINATED FURANS, EXPLOSIVES OR RADIOACTIVE MATERIALS. T09 - INCINERATION

# Container Contents

~~BULK~~

Lab Pack

RQ

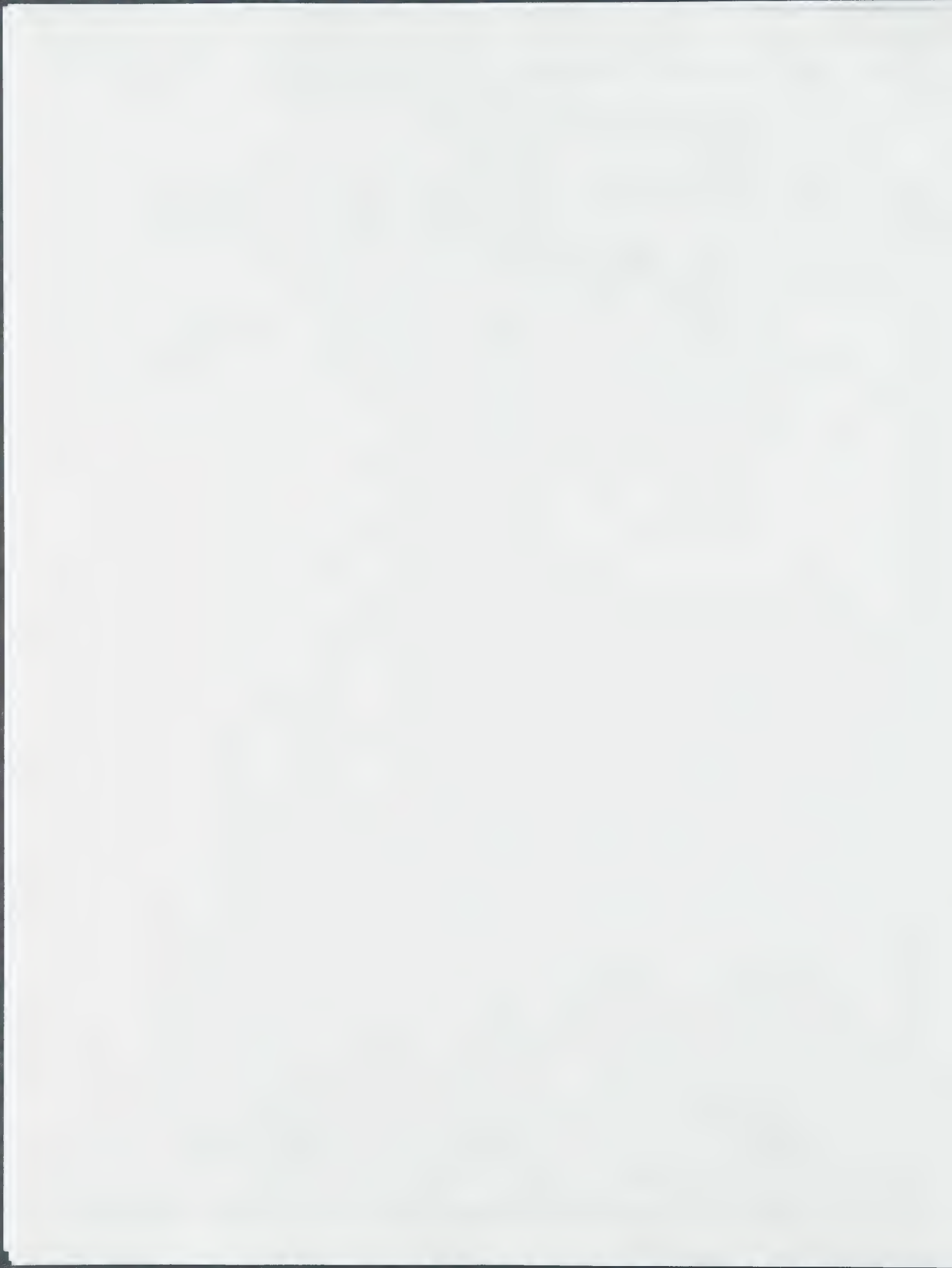
Container Number:	MONTH DAY YEAR	CODE	NUMBER	Chemist
DOT Shipping Name:	09 09 94	LR	8317-1516	TL
Container Type:	174	Size: S3	UN/NA Number: 2789	Absorbent 000
Hazard Class:	8 PGII			

Profile Number	<del>LABOR</del>
Disposal Site	PELITONICA
Approval Code	LP
Reactive WL	

Line No.	Material Description	PS	Material Quantity	I.C.	EPA Waste Code Number
01	GLACIAL ACETIC ACID	L	72 x 171	G	D002
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
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28					

ABSORBENT C - CORN COB V - VERMICULITE O - OTHER	PS - PHYSICAL STATE L - LIQUID / POURABLE S - SOLID X - SLUDGE	IC - INTERNAL CONTAINER G - GLASS M - METAL P - PLASTIC F - PAPER
This Lab Pack list continues: Yes <input type="checkbox"/> No <input type="checkbox"/>		This is page _____ of _____





Äther und Chloroform abgedampft und der Ester schließlich in ...

M

Er siedet unter 7 mm Druck bei 85°. Er ist nicht brennbar  
verpufft jedoch in porösen Substanzen aufgesaugt, ähnlich wie Ammonium  
nitrat im Capillarrohr schnell erhitzt, explodiert er mit großer  
Heftigkeit. In Wasser löst er sich schwer, zersetzt sich aber damit lang-  
sam schon bei gewöhnlicher Temperatur unter Bildung von Hydroxy-  
ester, Kohlensäure und Spuren von Stickstoffwasserstoff-  
säure. Diese wurde vor allem an ihrem heftigen Geruch, dann aber  
auch an einer geringen Menge von daraus darstellbarem Silberazid  
erkannt.

NB

Ergebnis 11 g (75% der Theorie)

Zersetzung von Azodicarbonsäure-diäthylester

10 g Azodimethylester werden mit 5 ccm 10%iger  
Salpetersäure versetzt und hierzu unter Eiskühlung 5 ccm rauchende  
Salpetersäure hinzugefügt. Wenn sich die Flüssigkeiten vermischt haben, g-  
ibt man 10 ccm Wasser hinzu. Die Lösung in 40 ccm Wasser von 30°. Unter lebhafter Gasentwicklung  
findet die Zersetzung statt, und nach einer Viertelstunde ist die Flüssigkeit  
schon gelblich geworden. Wird diese auf dem Wasserbade abgedampft, so  
bleibt ca. 1 g reines wasserfreie Oxalsäure, die sich zwischen 120° und  
130° zersetzt.

Aus Wasser umkristallisiert, schmilzt sie bei 101° die  
Kristallwasserhalt der Oxalsäure.

2. Methode: 10 g des Esters werden in einer Kältemischung vorsichtig  
mit 2 ccm gekühlter rauchender Salpetersäure versetzt, die man  
daran Schutteln vermischt und die rotgelbe Lösung im Eisschrank stehen  
überlassen. Es findet dabei eine langsame Gasentwicklung statt und nach  
2 Stunden hat sich die Lösung fast ganz entleert.

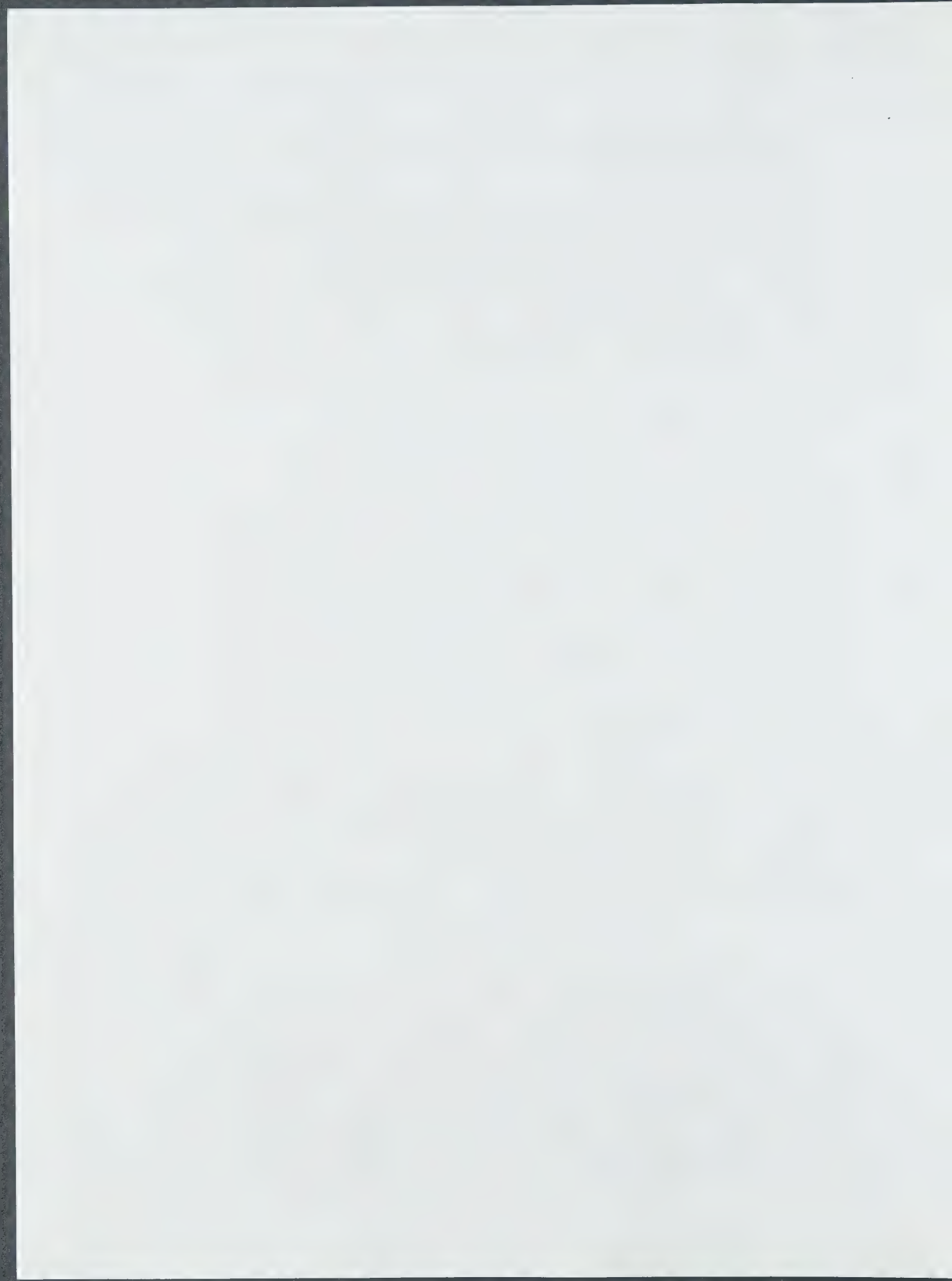
Im Vakuum verdampft, bleiben lange Prismen zurück, die  
als reine Oxalsäure erweisen.

Verbindung  $C_8H_{15}O_4N_2$

$C_8H_{15}O_4N_2$

Azodicarbonsäure-diäthylester und Dimethylamin

20 g Azodicarbonsäure-diäthylester werden mit 40 ccm Äther  
verdünnt, am Rückflußkühler zum Sieden erhitzt und langsam mit  
15 g einer 33-prozentigen Lösung von Dimethylamin in Äther  
versetzt. Die Flüssigkeit bleibt durch die Reaktionswärme im Sieden.  
Dann wird sie im Vakuum vollständig zur Trockne verdampft, der  
Rückstand dreimal mit wenig kaltem absolutem Äther gewaschen und  
endlich aus viel siedendem Äther umkristallisiert. Die Verbindung





Paper no. 256, Berichte, 1911, 44, pages 2007-2011  
New Compounds and Derivates of the Azodicarbonyl Group  
by Otto Diels and Max Paulin

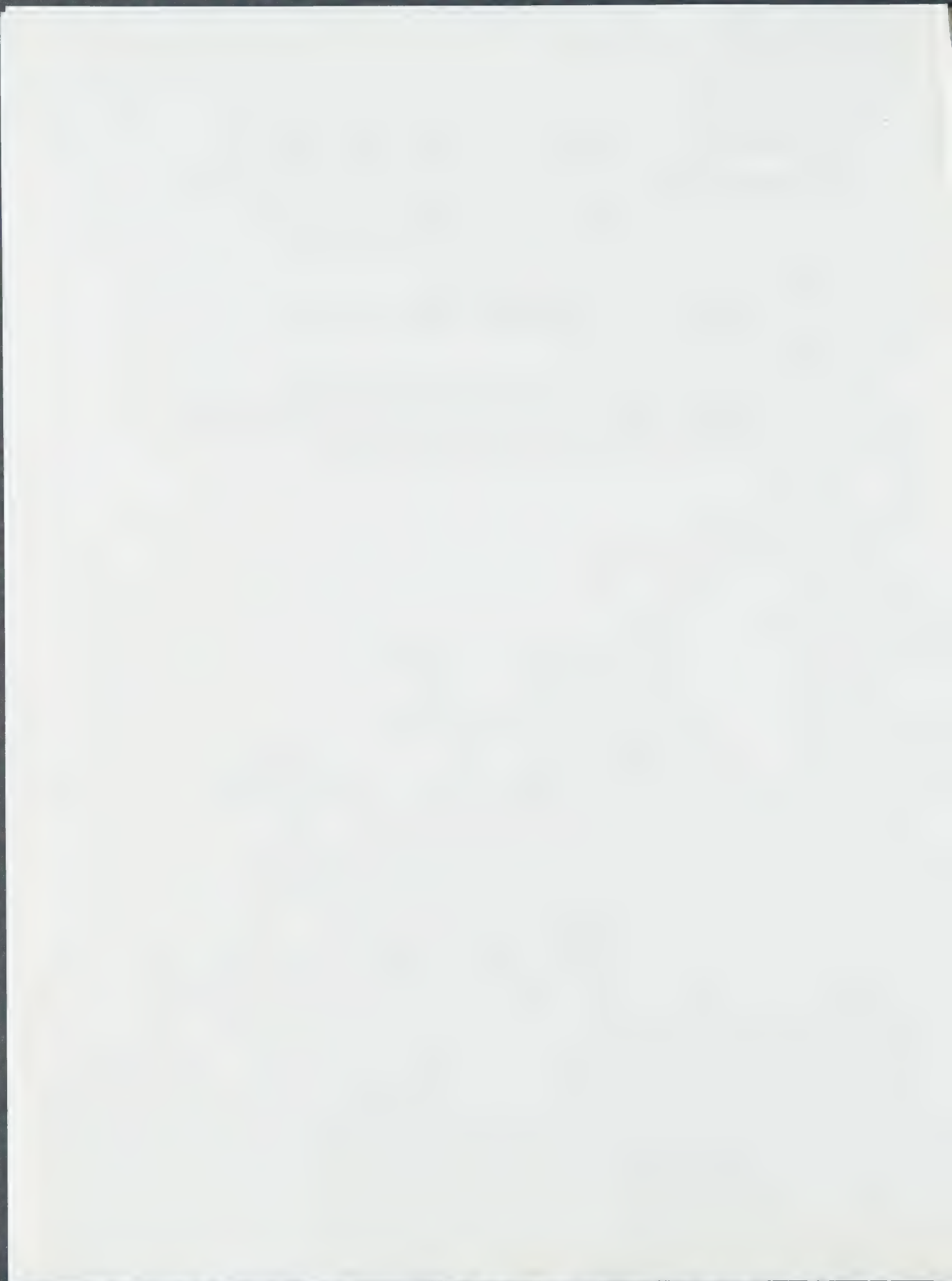
Section starting on page 2007  
Preparation of dimethylazodicarboxylic ester

Page 2008, lines 3 to 5:

It boils at 31 under 7 mm pressure. It does not burn,  
but when absorbed in porous substances and heated, it  
explodes like gunpowder. It explodes with great  
intensity when heated in a capillary tube.

Very - 117

but when absorbed in  
porous substances it  
goes pop like nitrocellulose.  
If heated quickly in a  
capillary, it explodes  
with great vigor!



in H<sub>2</sub>SO<sub>4</sub> with red color, etc. (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100) (101) (102) (103) (104) (105) (106) (107) (108) (109) (110) (111) (112) (113) (114) (115) (116) (117) (118) (119) (120) (121) (122) (123) (124) (125) (126) (127) (128) (129) (130) (131) (132) (133) (134) (135) (136) (137) (138) (139) (140) (141) (142) (143) (144) (145) (146) (147) (148) (149) (150) (151) (152) (153) (154) (155) (156) (157) (158) (159) (160) (161) (162) (163) (164) (165) (166) (167) (168) (169) (170) (171) (172) (173) (174) (175) (176) (177) (178) (179) (180) (181) (182) 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New Compounds and Reactions of the Azodicarboxylic Acids. O. K. ...

... explodes with great violence when heated, but ...

New Chemical Synthesis. HENRY PUTCHER AND R. SIMONIS. Ber. 40,





**1,10-DIMETHYL AZODIFORMATE**

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**DIMETHYL AZODIFORMATE**

mf: C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>, mw: 146.11

Shock-sensitive, burns explosively

**1,10-DIMETHYL-5,6-BENZACRIDINE**

CAS RN: 3518056 NIOSH #: CU 3510000

mf: C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>, mw: 200.24

SYN: 8,11-DIMETHYLBENZOCACRIDINE

**TOXICITY DATA:** 3 CODEN:  
 scu-mus TDLo 700 mg/kg/4W- ACPSAJ 4,315,56  
 I-E/A

*THR:* An exper E/A

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**2,10-DIMETHYL-5,6-BENZACRIDINE**

CAS RN: 17401488 NIOSH #: CU 3520000

mf: C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>, mw: 257.35

SYN: 9,12-DIMETHYLBENZOCACRIDINE

**TOXICITY DATA:** 3 CODEN:  
 kn-mus TDLo 540 mg/kg/45W- ACPSAJ 4,315,56  
 I-E/A

*THR:* An exper E/A

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**5,7-DIMETHYLBENZOCACRIDINE**

mf: C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>

**TOXICITY DATA:** CODEN:  
 mma-sat 20 ug/plate GANNA2 70,749,74

*THR:* MUT data

*Disaster Hazard:* When heated to decomp it emits toxic fumes

**7,9-DIMETHYLBENZOCACRIDINE**

CAS RN: 961993 NIOSH #: CU 348(XXX)

mf: C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>, mw: 257.35

SYN: 3,10-DIMETHYL-7,8-BENZACRIDINE (FRENCH)

**TOXICITY DATA:** 3 CODEN:  
 roma-sat 20 ug/plate PMASV6 12,155,71  
 otr-ham kdy 80 ug/l BJCAAI 37,873,71  
 sku-mus TDLo 180 mg/kg/15W- ACPSAJ 4,315,56  
 I-E/A  
 scu-mus TDLo 200 mg/kg/4W ACPSAJ 4,315,56  
 I-E/A  
 scu-mus TD: 250 mg/kg/10D I-E/A BAPEAG 34,22,47

*THR:* An exper E/A, MUT data

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**1,11-DIMETHYLBENZOCACRIDINE**

CAS RN: 3518056 NIOSH #: CU 3510000

mf: C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>, mw: 200.24

SYN: 1,11-DIMETHYLBENZOCACRIDINE (FRENCH)

**TOXICITY DATA:** 3 CODEN:  
 scu-mus TDLo 360 mg/kg/30W- ACPSAJ 4,315,56  
 I-E/A  
 scu-mus TDLo 200 mg/kg/4W- ACPSAJ 4,315,56  
 I-E/A  
 scu-mus TD: 250 mg/kg/10D I-E/A BAPEAG 34,22,47  
 GANNA2 70,749,74

*THR:* An exper E/A, MUT data

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**5,7-DIMETHYL-1,2-BENZACRIDINE**

CAS RN: 53690 NIOSH #: CU 3500000

mf: C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>, mw: 257.35

SYN: BENZACRIDINE (FRENCH)

**TOXICITY DATA:** 3 CODEN:  
 roma-sat 500 ug/plate ENMUDM 3,115  
 scu-mus TDLo 250 mg/kg/10D HAREAS 34,22,4  
 I-E/A  
 m-frg TDLo 11 mg/kg UNREAS 24,15,56  
 I-E/A

*THR:* An exper E/A, HIGH acute ivn, MUT data

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**6,9-DIMETHYL-1,2-BENZACRIDINE**

CAS RN: 2581400 NIOSH #: CU 348(XXX)

mf: C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>, mw: 257.35

SYN:

1,7-DIMETHYL-2,8-BENZACRIDINE (FRENCH)

**TOXICITY DATA:** 3 CODEN:  
 scu-mus TDLo 190 mg/kg/16W- ACR  
 I-E/A  
 scu-mus TDLo 60 mg/kg/4W- ACRSA  
 I-E/A  
 scu-mus TD: 150 mg/kg/10D I-E/A BAPEAG 34,22,47  
 BJCAAI 37,873,71  
 roma-sat 20 ug/plate UNREAS 24,15,56

*THR:* An exper E/A, MUT data

*Disaster Hazard:* When heated to decomp it emits toxic fumes of NO<sub>2</sub>

**N,N-DIMETHYLBENZAMIDE**

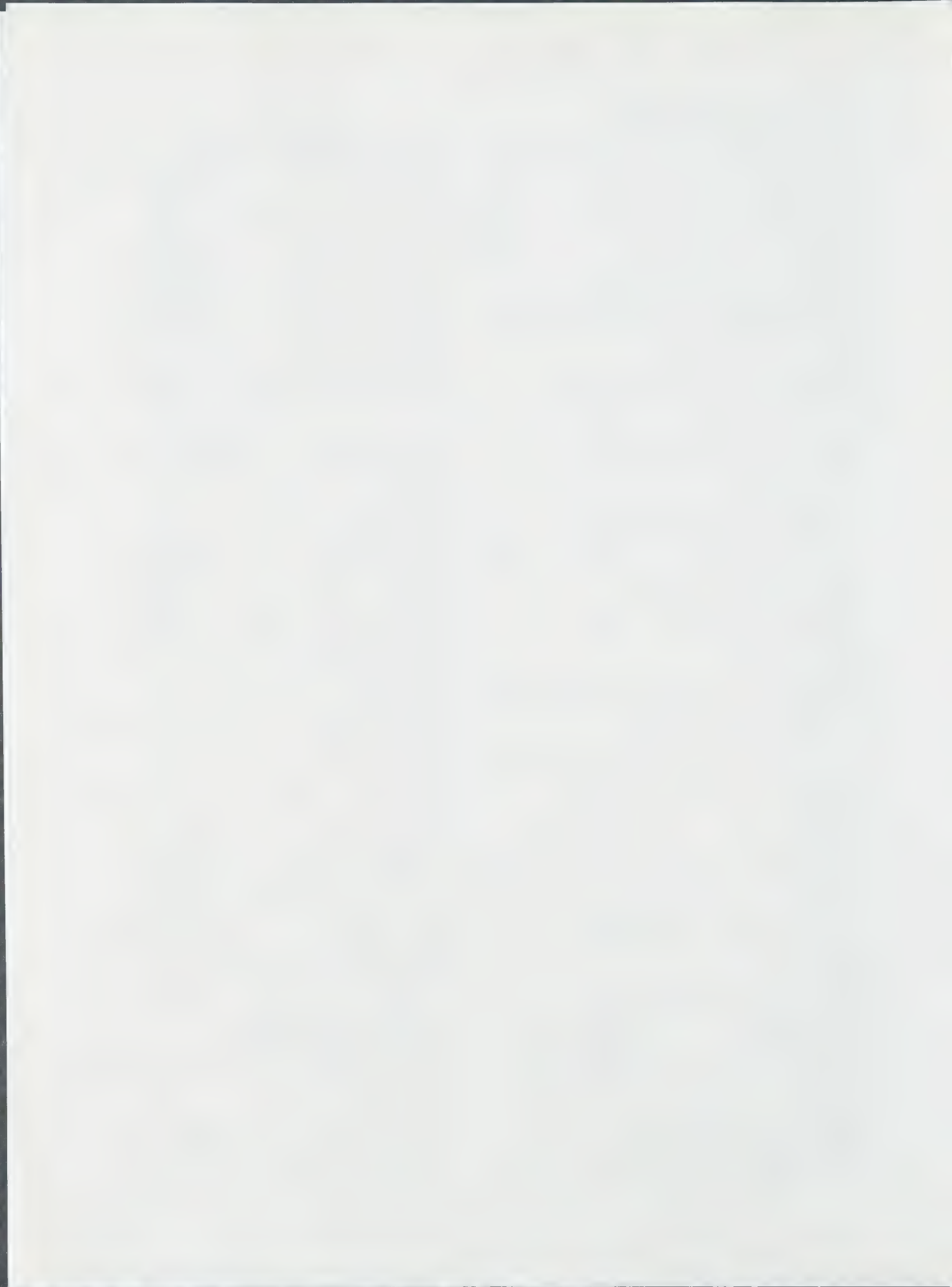
CAS RN: 611745 NIOSH #: CV 450000

mf: C<sub>7</sub>H<sub>11</sub>NO, mw: 149.16

SYN: DIMETHYLBENZAMIDE

**TOXICITY DATA:** 2 CODEN:  
 rat-mus LD50: 960 mg/kg TXAPA9 19,20

Reported in EPA TSCA Inventory, 1981





1

3,347,845  
**SHOCK STABLE AZODIFORMATE ESTERS**  
 Chester S. Sheppard, Kenmore, H. Norman Schack, Buffalo, and Orville L. Magell, Kenmore, N.Y., assignors to Wallace and Tiernan Inc., Buffalo, N.Y., a corporation of Delaware  
 No Drawing, Filed Dec. 9, 1963, Ser. No. 329,301  
 7 Claims. (Cl. 260-192)

**ABSTRACT OF THE DISCLOSURE**

A shock stable solution of certain azodiformates and inert organic liquid solvents. Examples: Dimethylazodiformate, 38%; dioctyl phthalate, 62%.

This is a continuation-in-part of our copending applications Ser. Nos. 299,152 and 299,161, filed Aug. 1, 1963, and both now abandoned.

This invention relates to certain esters of azodiformic acid. More particularly, it relates to compositions including these esters which are shock stable.

It is known that certain diesters of azodiformic acid (azodicarboxylic acid) are blowing agents for foaming polymers. It has been discovered, and this is disclosed in the above listed parent applications, that the blowing effectiveness of esters of azodiformic acid can be enhanced by the presence of an activating agent—a metallic compound having unneutralized Lewis acid properties. This defined ester-activator combination is of value in the production of foamed polymeric bodies, either thermoplastic or thermosetting polymers. Illustrative polymers include: the polyolefins such as polyethylene, polypropylene, synthetic rubber and natural rubber; the vinyl halides, such as polyvinyl chloride, and the copolymers such as vinyl chloride-vinyl acetate, the vinyl esters such as polyvinyl acetate, the cellulose esters, such as cellulose acetate, cellulose acetate butyrate, the cellulose ethers, such as methyl cellulose; the silicone gums and rubbers, the nitrile rubbers; the polyesters, saturated or unsaturated aliphatic and aromatic; the polyethers; the polyamides; the polyurethanes; the phenolic resins, and the epoxy resins. Any polymer may be foamed whose viscosity characteristics at the blowing temperature permit the expansion of the melt or the retention of the released gas.

The gas release efficiency per unit weight of these azodiformates is best with the lower molecular ester groups, such as dimethyl azodiformate and diethyl azodiformate. However, it has been discovered that these azodiformates are shock sensitive to a degree which probably bars them from use in commerce as blowing agents.

It has been discovered that an intimate mixture of a shock stable material, either liquid or solid, and a normally shock sensitive ester of azodiformic acid, in the proper proportions of material and ester, is shock stable to a degree permitting use as a "non-hazardous" polymer blowing agent. The ester group is either methyl, ethyl, allyl, butyl, hexylmethyl, alkylene oxyalkylene, thioalkylene where said alkylene groups have 2-4 carbon atoms. The diester may be a simple azodiformate, or an ester group bridged by azodiformate, or a polyester having three or more repeating "azo" units.

The terms "shock sensitive" and "shock stable" are used herein relative to the standard dropping weight and lead pipe deformation tests described by Noller and Bolton, "Analytical Chemistry," 35, 889 (1963). Briefly, in the LPD test, 10 grams of test material are placed in a glass tube, a No. 6 electrical blasting cap positioned in the material, the tube is placed in a close fitting lead pipe and the cap is detonated. The condition of the pipe determines the classification of the material.

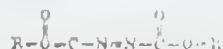
2

The azodiformates which come within the scope of this invention are diesters of azodiformic acid or realtive thereof containing the



unifunctional group

(a) The diesters present in the composition of the invention may be the simple diesters of azodiformic acid having the formula:



where R is an "ester group" from the class of methyl, ethyl, allyl, or hexylmethyl. Illustrative simple diesters are dimethyl azodiformate; diethyl azodiformate, and diallyl azodiformate.

(b) The diesters include two "azo" groups bridged by a difunctional ester group from the class of alkylene, oxyalkylene, thioalkylene, where these alkylene groups have 2, 3 or 4 carbon atoms. Illustrative groups are ethylene ( $-\text{CH}_2\text{CH}_2-$ ); propylene ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ); n-butylene; oxydiethylene ( $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$ ); and thiodiethylene ( $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-$ ). This class of the diesters which come within the scope of the invention is illustrated by ethylene bis(methylazodiformate):



(c) The diesters include polyester condensates from the reaction of the difunctional azodicarboxylic group donor and a difunctional ester group donor. For example, these diesters may be visualized as the polyester condensation products, having at least three "azo" units, of azodiformic acid and a glycol having 2-4 carbon atoms. A building block repeating unit may be written for the  $-\text{CH}_2\text{CH}_2-$  ester group as follows:



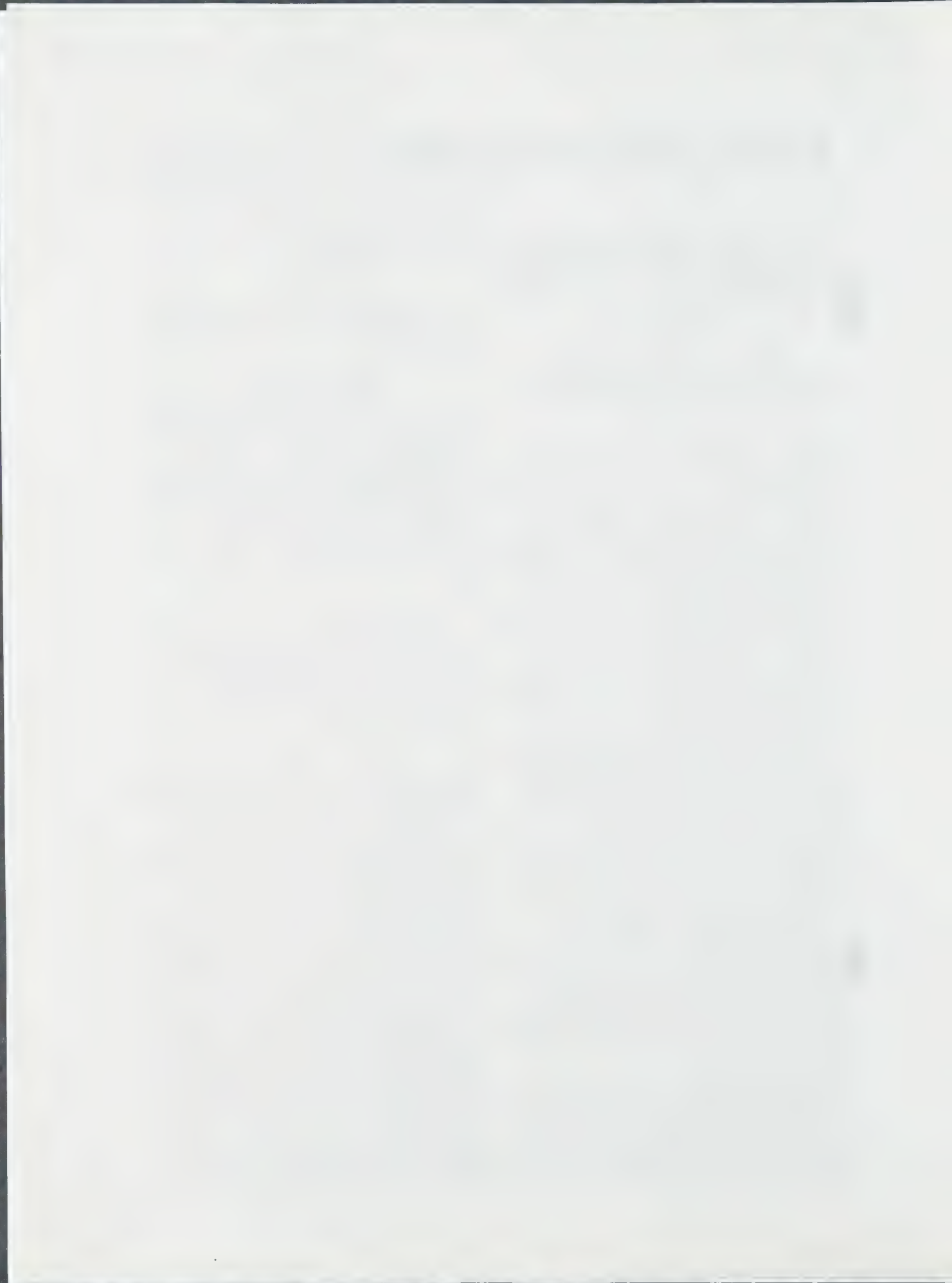
In the polyester product, at least three units are present. The chain length is desirably controlled by introducing into the polyester condensation reaction zone a stopper compound which is a donor of a monofunctional ester group either methyl, ethyl, allyl, or hexylmethyl.

Typical azodiformates are: dimethyl, an orange liquid, d. 190° C.; diethyl, an orange liquid, boils about 240° C.; diallyl, an orange liquid, tends to polymerize on heating; diethylene bis(ethyl azodiformate) a red liquid.

The composition of the invention consists essentially of an intimate mixture of a shock stable material and one or more of the normally shock sensitive diesters defined above, in proportions such that the mixture is shock stable. The mixture may be a solution, i.e. a homogeneous mixture, or a heterogeneous mixture, such as a solid diester mixed with a solid material or coated on the solid material or a liquid diester adsorbed on a solid carrier.

The proportion of material and diester in the composition will be dependent on the diester, mainly the material, and the degree of shock stability desired. Very broadly, a practical degree of shock stability is present when the composition includes the material and the diester in a weight proportion of at least about 15:85, i.e. at least about 15 parts by weight of the shock stable material is present per 100 parts of material plus diester present in the composition.

One embodiment of the composition of the invention utilizes as the shock stable material a liquid solvent for the diester. Any organic liquid which is not shock sensitive and which possesses the requisite solubility in or for the particular diester and does not react therewith may be



used, e.g. shock stable azodiformate diesters. Any of the liquids commonly known as organic solvents may be used in the composition of the invention: to illustrate, aliphatic hydrocarbons—paraffins, cycloparaffins and aromatics—such as pentane, heptane, cyclohexane, benzene and toluene, monohydric alcohols, such as methanol, ethanol and isopropanol; polyhydric alcohols and ether alcohols; esters; ketones; halogenated hydrocarbons such as methyl chloride and carbon tetrachloride; heterocyclic solvents such as tetrahydrofuran; the ester solvents such as ethyl acetate.

Especially advantageous solvents are those materials which are plasticizers for one or more of the polymers used in the preparation of cellular bodies. The diester may be conveniently dissolved in the plasticizer used in the preparation of the plastisol to be foamed; this solution is more easily blended into the plastisol and does not require the subsequent removal of solvent. Illustrative plasticizers are: the phthalates: dioctyl, dicapryl, diisodecyl, diallyl, butyl benzyl, and dimethyl Cellosolve; the sebacates: dibutyl, dihexyl, and dioctyl; triethyl citrate; tricresyl phosphate; chlorinated biphenyls; epoxy type plasticizers.

The minimum amount of organic solvent needed to impart a reasonable degree of shock stability to the composition will be dependent mainly on the type of diester. In general, compositions having a minimum degree of hazard are attained with solution weight proportions of solvent to diester of about 25-65; 75-35. At one end of this general range, 25 parts by weight of solvent are present in 100 parts of solvent plus diester; at the other end of the range about 65 parts by weight of solvent are present in 100 parts of solvent plus diester.

Heterogeneous mixtures involving a solid material are effective in producing shock stable compositions. When the diester is a solid, an intimate mixture of finely divided diester solid and finely divided shock stable solid material is desirable. Any solid which is shock stable and inert toward the diester may be used. In some instances the diester may be sufficiently finely divided to form a coating on the larger sized solid material, giving a mixture which does not segregate on storage.

In the case of the liquid diesters it is preferred to adsorb the liquid on a solid carrier; this may be purely surface adsorption on a finely divided solid or it may be adsorption by a porous solid.

Illustrative shock stable solid materials are: silica, silica gel; and particularly the silica aerosols; charcoal; carbon black; diatomaceous earth such as kieselguhr; perlite; natural clays such as kaolin, bentonite and fuller's earth; synthetic clays; crystalline porous zeolites; alumina; talc; aluminum silicate; titanium dioxide and calcium carbonate.

As with the liquid solvents, the solid materials are used in at least the amount needed to obtain a reasonably shock stable composition. In general, the solid carrier-diester mixture has weight proportions of solid to diester of about 25-65; 75-35; in other words at one end of the range 25 parts by weight of solid carrier are present for 100 parts of carrier plus diester; at the other end of the range about 65 parts by weight of carrier are present for 100 parts of carrier plus diester.

The solid composition is particularly advantageous in the foaming of polymers which do not require a plasticizer such as rubber and polyethylene. The solid composition is readily milled into the polymer to obtain a uniform dispersion of the composition which uniformity is necessary for the production of a satisfactory cellular structure in the foam.

The composition of the invention includes liquid-liquid and solid-liquid mixture wherein the diester is intimately dispersed through a liquid medium in which the diester is substantially insoluble. Some of the less common plasticizers exhibit low solubility for these diesters; this dispersion composition permits ready milling of the diester into the polymer using this plasticizer. This dispersion

composition permits the use of the diester in connection with inorganic liquids such as water.

#### ILLUSTRATIONS

The invention is illustrated by several compositions. It is to be understood that these illustrative compositions do not limit the scope of the invention.

#### Dimethyl azodiformate

(1) In the standard drop test, a 0.03 milliliter test amount of the dimethyl azodiformate was struck by a one-gram weight in a one-half inch fall. The diester detonated with a very loud report.

(2) Two small drops of this diester were placed in a dish and a flame applied directly thereto. The drops ignited and instantaneously exploded with a loud report. These tests and others establish that this diester is a maximum hazard explosive and therefore barred by ICC regulations from transport by any common carrier.

(3) A solution of 80 weight percent of this diester and 20 weight percent of dioctyl phthalate was prepared. In the drop test, the test sample did not detonate at the 10-inch drop height.

(4) A solution of 85 percent of this ester and 15 percent of benzene was shock stable at the 10-inch height in the drop test.

(5) A solution of 90% of this ester and 10% of methylene chloride was shock stable at the 10 inch height in the drop test.

(6) A solution of 38 percent of this diester in 62 percent of dioctyl phthalate was shock stable in the lead pipe detonation test—giving the same deformation of the pipe as does water in this test.

(7) A 50:50 weight proportion solid mixture of this diester and silica aerosol (Cab-O-Sil) was prepared. This composition was shock stable in both the drop test and the lead pipe detonation test.

(8) A 50:50 weight proportion solid mixture of this diester and diatomaceous earth was prepared. This composition was shock stable in both the drop test and the lead pipe detonation test.

#### Diethyl azodiformate

(9) Diethyl azodiformate was found in the lead pipe detonation test to behave like ammonium nitrate. This makes it an ICC Class A, type 5, explosive.

(10) A solution of 90 weight percent of this diester and 10 weight percent of dioctyl phthalate could not be detonated in the lead pipe detonation test—this solution behaved like water.

(11) A 50:50 weight proportion solid mixture of this diester and Cab-O-Sil silica was shock stable in the lead pipe detonation test.

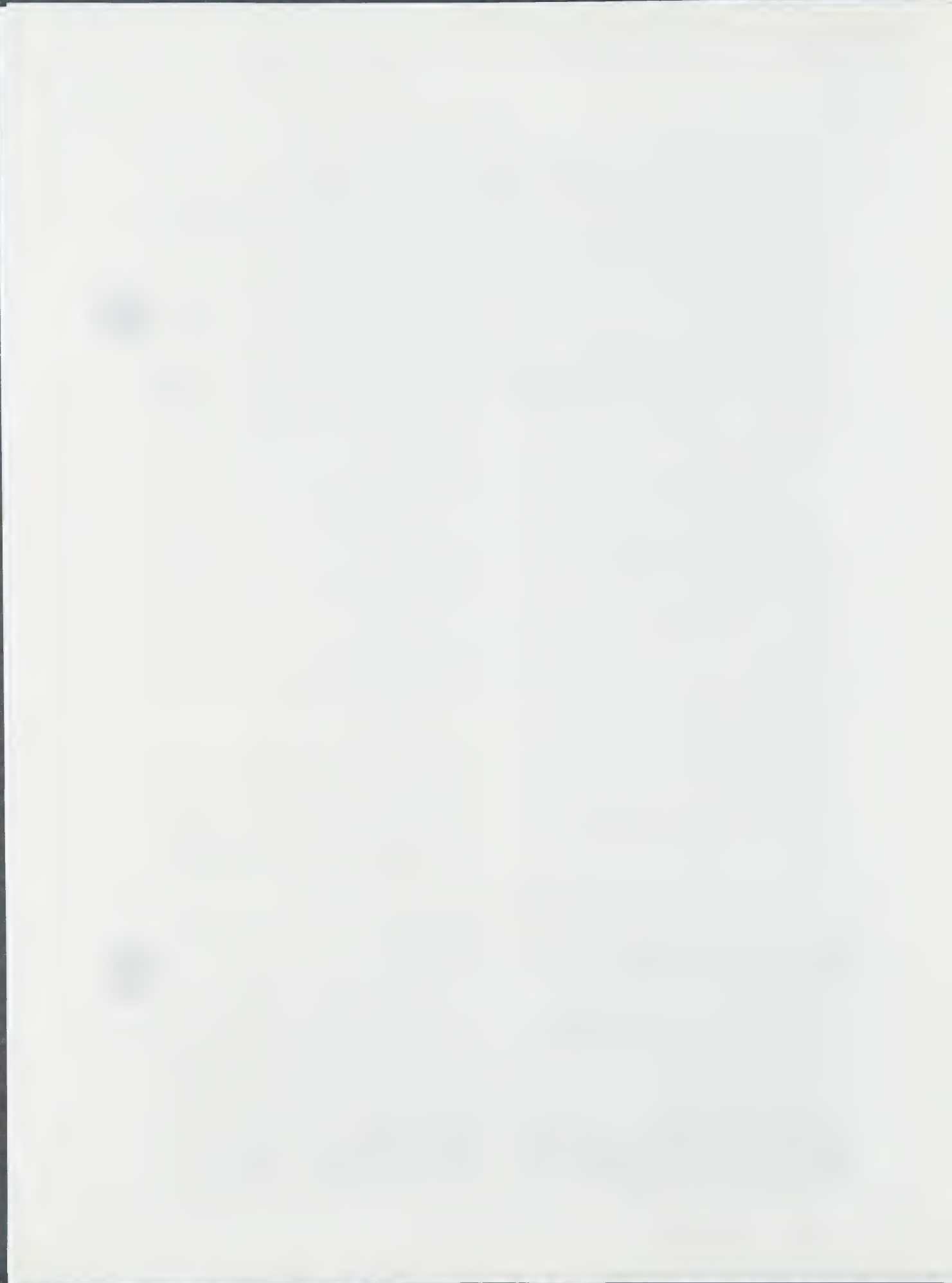
#### PREPARATIONS

These diesters can be prepared by several prior art techniques; summaries of which are given in the parent application. A preferred method of preparing dimethyl azodiformate is set out.

#### Preparation of dimethyl azodiformate

The entire reaction for making 454 grams of dimethyl azodiformate was carried out in a 5-liter reaction glass reactor kettle that was jacketed for cooling and that was equipped with a bottom drain valve for separating and removing liquid layers. The reactor kettle was charged with a solution containing 105.7 grams of 1% formalin in 1500 ml. of water. The solution was cooled to about 10° C. by circulating cold water through the jacket of the reactor. While maintaining efficient stirring the addition of 671 grams of 97.5% pure methyl chloroformate was started. The reaction is exothermic and sufficient cooling was used to maintain a reaction temperature of 10° C. ± 2° C. When one-half of the methyl chloroformate (336.5 grams) had been added, the addition of 367.6 grams of sodium carbonate powder was begun, suultane





ous with the chloroformate. The rate of the sodium carbonate addition was controlled so that the methyl chloroformate addition was completed somewhat in advance of the sodium carbonate addition. A reaction temperature of  $10^{\circ} \pm 2^{\circ}$  C. was maintained throughout these additions. The total addition time was about one hour.

After stirring for an additional 15 minutes, 786 ml of methylene chloride was added. With the reaction mixture maintained at  $0-5^{\circ}$  C., chlorine gas was admitted to the stirred reaction mixture as fast as it could be completely absorbed. After a total of 258.0 grams of chlorine was admitted, the chlorine addition was discontinued. The reaction mixture was stirred for an additional 10 minutes and then the two layers were allowed to separate.

The lower orange colored methylene chloride layer was drawn off. The aqueous layer was washed with 120 ml. of methylene chloride. This wash layer was drawn off and combined with the first methylene chloride layer. The aqueous layer was discarded. The combined methylene chloride layers were washed with 250 ml. of a 10% sodium chloride solution and then with 500 ml. of 10% sodium bicarbonate solution. The solution was then dried over anhydrous sodium sulfate and filtered. The methylene chloride solvent was then removed under vacuum (20 mm. of Hg) at  $40^{\circ}$  C. to obtain 454 grams of dimethyl azodiformate of approximately 97.5% purity.

#### Preparation of a bridged diester

The ester of diethylene glycol with monoethyl azodiformate, or diethylene bis(ethyl azodiformate), was prepared according to the procedure described by N. Rabjohn in the *Journal of the American Chemical Society*, vol. 70, page 1182 (1948). Diethylene glycol was treated with phosgene to obtain the bis(chloroformate). This product was treated with ethyl carbazate (prepared from diethyl carbonate and 85% hydrazine hydrate) to obtain the diethylene bis(ethyl hydrazodiformate), which subsequently was oxidized with aqueous chlorine to the corresponding azodiester. This diester is a red, clear liquid

The infrared spectrum and hydrogen iodide titration show that the diester was obtained in quite pure form.

Thus having described the invention, what is claimed is:

1. A shock stable solution composition consisting essentially of inert organic liquid solvent for hereinafter said diester and a normally shock sensitive diester of azoformic acid where the ester groups are selected from the class consisting of methyl, ethyl, allyl, alkylene, cycloalkylene, thioalkylene, said alkylene group having 2-4 carbon atoms; said solvent and said diester being present in weight proportions ranging between about 15:85 and about 65:35.
2. The solution of claim 1 wherein said diester is selected from the class consisting of dimethyl azodiformate, diethyl azodiformate, diethylene bis(ethyl azodiformate), diethylene bis(methylazodiformate).
3. The solution of claim 1 wherein said solvent is selected from the class consisting of methanol, methylene chloride, dioctyl phthalate, dibetyl sebacate and triethyl phosphate.
4. The solution of claim 1 wherein said proportions are between about 25:75 and about 65:35.
5. A shock stable composition consisting of about 38-80 weight percent of dimethyl azodiformate and about 62-20 weight percent of dioctyl phthalate.
6. A shock stable composition consisting of about 10 weight percent of methylene chloride and about 90 weight percent of dimethyl azodiformate.
7. A shock stable composition consisting of about 10 weight percent of dioctyl phthalate and about 90 weight percent of diethyl azodiformate.

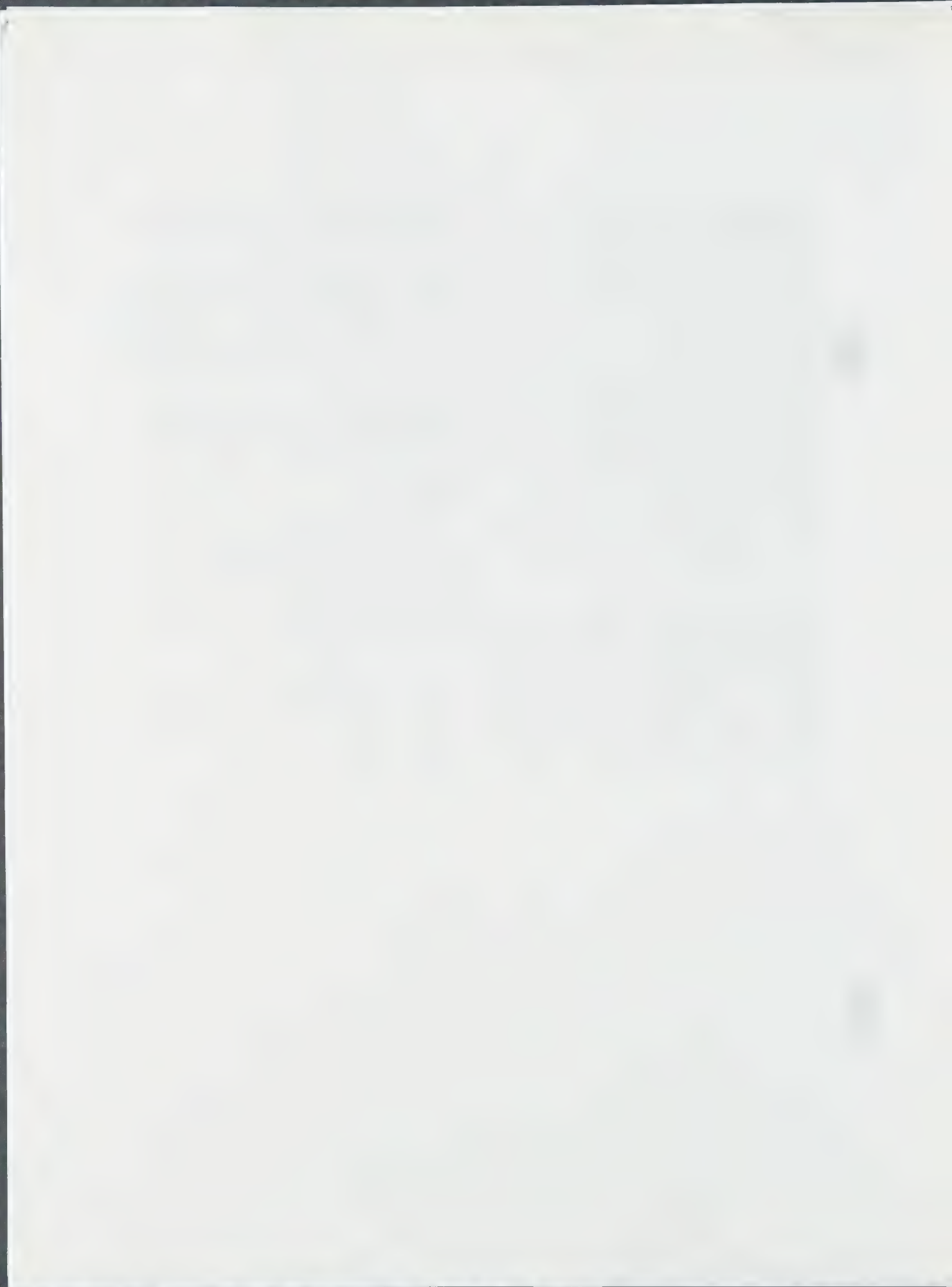
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HARLES B. PARKER, *Primary Examiner*

D. HIGEL, *Assistant Examiner*





- 3) Trinitrotoluene will be set off by exposure to ...
- ... will detonate in 1000 sec at 160° or in 0.1 ...
- ... acid will detonate in 9 sec at 300° or ...

An explosion of HE may also be initiated by severe shock. Sensitivity of explosives to shock may be measured in several ways, such as the impact pendulum method and the drop test. The impact pendulum test operates by allowing a heavy pendulum to swing down over a sample of explosive in a dished, cylindrical container so arranged that there is very little surface area between the pendulum and the sample. Thus the effect of contact between the sample and the pendulum bob is one of a combination of shock and pressure. The height from which the pendulum is allowed to swing to explode the sample is a measure of the sensitivity of the sample to this test. The drop test consists of placing a sample upon an anvil and allowing a weight to drop on it. The height from which the weight must drop to explode the sample is a measure of the sample's sensitivity to shock.

Below is a table of the results of a drop test upon various samples. These results must be considered as approximate and not by any means absolute. Solid explosives are in dished, cylindrical containers, unless otherwise noted.

- 1) mercury fulminate = 2 in. at 5 lbs
- 2) glycerin = 4 in. at 5 lbs.
- 3) tetryl = 8 in. at 5 lbs
- 4) nitric acid = 14 in. at 5 lbs
- 5) trinitrotoluene = 20 in. at 5 lbs
- 6) lead azide (a low explosive) = 30 in. at 5 lbs.\*

\*From Explosions: Their Anatomy and Destruction by C. S. Robinson (McGraw-Hill)

The most important test for explosives is the speed at which a detonation wave travels. This speed is usually in the range of 1000 to 3000 m/sec. Speed of detonation is found to be dependent upon kind of explosive and state of compaction.

There is an optimum state of compaction at which the explosive tends to become "dead-ended," in which state it is difficult to make the whole sample explode. Below the point of optimum compaction the rate of detonation is found to be directly proportional to the density of the sample. Below are some maximum detonation rates, in meters per second, for some common explosives.

glycerin	8500
DTN	8100
tetryl	7700
nitric acid	7400
trinitrotoluene	7400
lead azide	4900

mercury fulminate	4800
ammonium nitrate	1100
low explosives	1000

It has been found that upon detonation an explosive can cause a nearby sample of explosive to detonate "sympathetically." The distance over which one charge can detonate another is a function of the amount of energy produced by the first explosion and the medium through which the shock wave is propagated to the second charge of explosive. For instance the relationship for air (very approximately) would be expected to be: Weight of explosive in lbs. (distance in ft)<sup>2</sup> = 4. Thus to calculate the maximum distance for a possible sympathetic detonation of 40,000 lbs of explosive, the calculation is:

$$W = 4 \times D^2$$

$$40,000 = 4 \times D^2$$

$$D = 22 \text{ ft (approximately)}$$

According to C. S. Robinson the formula is more nearly

$$\text{weight of explosive} = 4 \times (\text{distance})^{2.2}$$

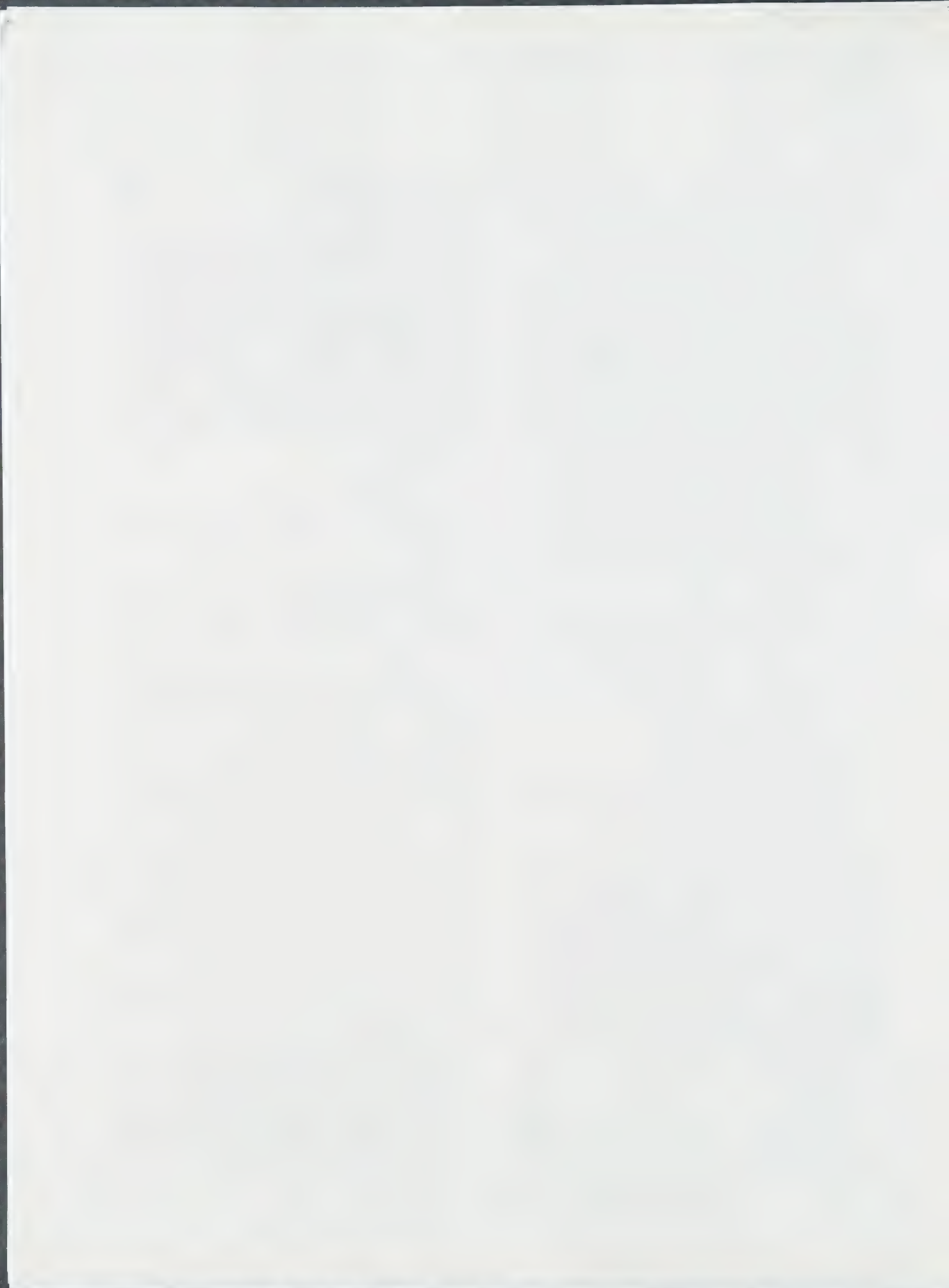
The power of the shock wave is much more rapidly attenuated in water, wood, etc., than in air, which means that if a shield of water or wood is interposed between piles of explosive the distance between them may be lessened.

**Liquid Oxygen.** Though not by itself explosive liquid oxygen can be dangerous when blended with highly flammable or carbonaceous materials. In this combination it is used in coal mining, quarrying, strip mining, and open-cut ore mining, and in rocket fuels. Its use underground or in confined places is not recommended by the U.S. Bureau of Mines, because it evolves a lot of carbon monoxide. (See carbon monoxide). This type of explosive has many safety advantages. For instance it is not itself an explosive until mixed with a flammable material which can be done at the last moment before firing. However, once an explosive has been made up, it is very flammable and will catch fire it will usually detonate. Liquid oxygen explosives are not stored, as they deteriorate rapidly and lose a great deal of their explosive power in a short time.

**General Fire Hazard:** Severe, when exposed to heat or by chemical reaction with powerful oxidizing agents.

**General Explosion Hazard:** Mod to dangerous when severely shocked or heated, depending upon kind of explosive, state of compaction, degree of confinement, etc. Practically all high explosives used commercially require a detonator or cap to set them off as compared to an igniter needed to set off black blasting powder (See also Explosives, Permissible

For more detailed information and Abbreviations see the Directory at the Beginning of this Section



(2) A chemical that has a median lethal dose (LD<sub>50</sub>) of more than 200 milligrams per kilogram, but no more than 1000 milligrams per kilogram of body weight when administered by continuous contact for 24 hours (or less, if death occurs within 24 hours) with the bare skin of albino rabbits weighing between 2 and 3 kilograms each.

(3) A chemical that has a median lethal concentration (LC<sub>50</sub>) in air of more than 200 parts per million (ppm), but no more than 2000 parts per million (ppm) of gas or vapor by volume, or more than 2 milligrams per liter, but no more than 20 milligrams per liter, of mist, fume, or dust, when administered by continuous inhalation for 1 hour (or less, if death occurs within 1 hour) to albino rats weighing between 200 and 300 grams each, provided such concentration or condition, or both, are likely to be encountered by man when the chemical is used in any reasonably foreseeable

**vapor** The gaseous form of a chemical that may diffuse and that is normally in the solid or liquid state

#### 4 General Requirements

4.1 A hazardous chemical shall be labeled for its immediate and delayed hazards. These hazards are its reasonably foreseeable physical hazards and its reasonably foreseeable health hazards as determined by a health hazard evaluation. (See Section 5.)

4.2 The following subject matter shall be considered for inclusion on precautionary labels: (1) identification of the chemical product or its hazardous component(s); (2) signal word; (3) statement(s) of hazard(s); (4) precautionary measures; (5) instructions in case of contact or exposure; (6) antidotes; (7) notes to physicians; (8) instructions in case of fire and spill or leak; and (9) instructions for container handling and storage.

4.2.1 Identification of the chemical product or its hazardous component(s) shall be adequate to allow selection of proper action in case of exposure. Identification shall not be limited to a nondescriptive code designation or trade name. For a single chemical substance the chemical name shall be used. For mixtures, the chemical names of the components contributing substantially to the hazards of the mixture shall be included as part of the label. In some instances, this information may be a trade secret or proprietary. In such instances, this information need not be included on the label; however, a procedure shall be available to provide information in emergency situations. In all cases, the appropriate precautionary labeling must be shown.

4.2.2 The signal word shall indicate the relative degree of severity of an immediate hazard in diminishing order: DANGER!, WARNING!, and CAUTION!. When a chemical has more than one hazard, only the signal word corresponding to the class of greatest immediate hazard shall be used. In differentiating immediate from delayed hazards by the optional use of a signal word for delayed hazards, it is recommended that a signal word other than one of those cited above be selected.

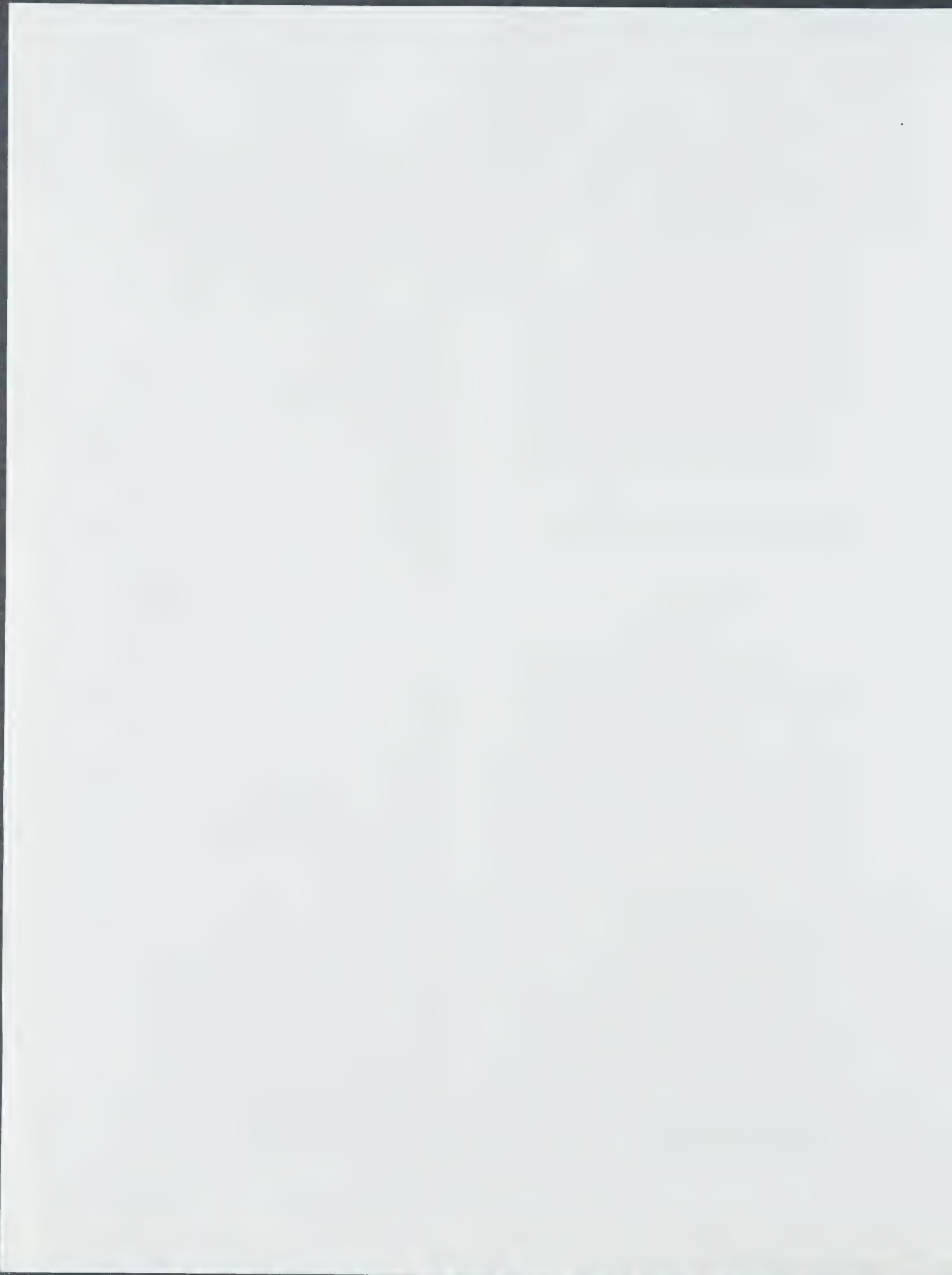
4.2.3 For highly toxic chemicals, additional attention shall be directed to the potentially severe harm that may result from exposure to these chemicals by the use of the word POISON and by the use of the skull and crossbones symbol placed above the instruction in case of contact or exposure. This legend, when used, shall not replace the signal word.

4.2.4 The statement of hazard shall give notice of hazard or hazards (for example, EXTREMELY FLAMMABLE and HARMFUL IF ABSORBED THROUGH SKIN) that are present in connection with the customary or reasonably foreseeable handling or misuse of the chemical. For chemical products with more than one immediate hazard, an appropriate statement for each significant hazard shall be included. Because immediate hazards are more likely to be the result of single exposures, they should usually precede the statements of hazards for delayed hazards. In general, the most serious immediate hazard shall be placed first, followed by all other immediate hazards. It is desirable to group delayed hazards. Hazards listed as immediate need not be repeated in the delayed hazards section.

4.2.5 The precautionary measures (for example, keep away from heat, sparks, and flame and avoid breathing dust) shall supplement the statements of hazards by briefly providing measures to be taken to avoid injury from the hazard or hazards.

4.2.6 Instructions in case of contact or exposure shall be included where the results of contact or exposure warrant immediate treatment (first aid), and where simple remedial measures may be taken before professional medical assistance is available. Procedures recommended for providing assistance shall be limited to those that may be expected of individuals without special training. Simple remedial measures (such as washing or removal of clothing) shall be included where they will serve to lessen or avoid serious injury following contact or exposure. This section on the label shall be captioned: FIRST AID (see 5.7 for first aid statements). When specific antidotes are known and are of such a type that may be administered by a person without training, they shall be included on the label with the caption: ANTIDOTE (see 5.8). Antidotes or





which is considered to be a carcinogen under paragraph (d)(4) of this section.

(3) If a mixture has not been tested as a whole to determine whether the mixture is a physical hazard, the chemical manufacturer, importer, or employer may use whatever scientifically valid data is available to evaluate the physical hazard potential of the mixture and:

- (iv) If the chemical manufacturer, importer, or employer has evidence to indicate that a component present in the mixture in concentrations of less than one percent (or in the case of carcinogens less than 0.1 percent) could be released in concentrations which would exceed an established OSHA permissible exposure limit or ACGIH Threshold Limit Value, or could present a health hazard to employees in those concentrations, the mixture shall be assumed to present the same hazard.

(6) Chemical manufacturers, importers, or employers evaluating chemicals shall describe in writing the procedures they use to determine the hazards of the chemical they evaluate. The written procedures are to be made available, upon request, to employees, their designated representatives, the Assistant Secretary and the Director. The written description may be incorporated into the written hazard communication program required under paragraph (e) of this section.

(4) Written hazard communication program. (1) Employers shall develop, implement, and maintain at the work place, a written hazard communication program for their workplaces which at least describes how the criteria specified in paragraphs (f), (g), and (h) of this section for labels and other forms of warning, material safety data sheets, and employee information and training will be met, and which also includes the following:

- (i) A list of the hazardous chemicals known to be present using an identity that is referenced on the appropriate material safety data sheet (the list may be compiled for the workplace as a whole or for individual work areas); and
- (ii) The methods the employer will use to inform employees of the hazards of non-routine tasks (for example, the

cleaning of reactor vessels), and the hazards associated with chemicals contained in unlabeled pipes in their work areas.

(2) Multi-employer workplaces. Employers who produce, use, or store hazardous chemicals at a workplace in such a way that the employees of other employers may be exposed (for example, employees of a construction contractor working on site) shall additionally ensure that the hazard communication programs developed and implemented under this paragraph (e) include the following:

- (i) The methods the employer will use to provide the material safety data sheet, or to make it available at a central location in the workplace, for each hazardous chemical, the other employer(s) employees may be exposed to, while working;
- (ii) The methods the employer will use to inform the employer(s) of any precautionary measures that need to be taken to protect employees during the workplace's normal operating conditions and in foreseeable emergencies; and
- (iii) The methods the employer will use to inform the other employer(s) of the labeling system used in the work place.

(3) The employer may rely on an existing hazard communication program to comply with these requirements, provided that it meets the criteria established in this paragraph (e).

(4) The employer shall make the written hazard communication program available, upon request, to employees, their designated representatives, the Assistant Secretary and the Director, in accordance with the requirements of 29 CFR 1910.20(e).

(5) Labels and other forms of warning. (1) The chemical manufacturer, importer, or distributor shall ensure that each container of hazardous chemicals leaving the workplace is labeled, tagged or marked with the following information:

- (i) Identity of the hazardous chemical(s);
- (ii) Appropriate hazard warnings; and
- (iii) Name and address of the manufacturer or other responsible party.

(2) The methods the employer will use to inform employees of the hazards of non-routine tasks (for example, the

cleaning of reactor vessels), and the hazards associated with chemicals contained in unlabeled pipes in their work areas.

(2) Multi-employer workplaces. Employers who produce, use, or store hazardous chemicals at a workplace in such a way that the employees of other employers may be exposed (for example, employees of a construction contractor working on site) shall additionally ensure that the hazard communication programs developed and implemented under this paragraph (e) include the following:

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- (ii) The methods the employer will use to inform the employer(s) of any precautionary measures that need to be taken to protect employees during the workplace's normal operating conditions and in foreseeable emergencies; and
- (iii) The methods the employer will use to inform the other employer(s) of the labeling system used in the work place.

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- (i) Identity of the hazardous chemical(s);
- (ii) Appropriate hazard warnings; and
- (iii) Name and address of the manufacturer or other responsible party.

establishing that the chemicals listed in paragraph (d)(4) of this section are hazardous.

(1) 29 CFR Part 1910, Subpart Z, and the Hazardous Substances Classification and Health Administration (OSHA); or

(2) Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment, American Chemical Society (AICHE) (latest edition).

The chemical manufacturer, importer, or employer is still responsible for evaluating the hazards associated with the chemicals in these source lists in accordance with the requirements of this standard.

(4) Chemical manufacturers, importers and employers evaluating chemicals shall treat the following sources as establishments that a chemical is a carcinogen or potential carcinogen for hazard communication purposes:

- (i) National Toxicology Program (NTP);
- (ii) Annual Report on Carcinogens (latest edition);
- (iii) International Agency for Research on Cancer (IARC) Monographs (latest edition); or
- (iv) 29 CFR Part 1910, Subpart Z, Toxic and Hazardous Substances, Occupational Safety and Health Administration.

Note: The Registry of Toxic Effects of Chemical Substances published by the National Institute for Occupational Safety and Health indicates whether a chemical has been found by NTP or IARC to be a potential carcinogen.

(5) The chemical manufacturer, importer or employer shall determine the hazards of mixtures of chemicals as follows:

- (1) If a mixture has been tested as a whole to determine its hazards, the results of such testing shall be used to determine whether the mixture is hazardous.
- (2) If a mixture has not been tested as a whole to determine whether the mixture is a health hazard, the mixture shall be assumed to present the same health hazards as do the components which comprise one percent (or, in the case of carcinogens, less than 0.1 percent) of the mixture, except that the mixture shall be assumed to present a health hazard if it contains a component known to be a carcinogen in a concentration of greater than 0.1 percent or greater than 1 percent, or greater

than 1 percent, of the mixture.

(3) The chemical manufacturer, importer, or employer shall determine the hazards of mixtures of chemicals as follows:

- (i) If a mixture has been tested as a whole to determine its hazards, the results of such testing shall be used to determine whether the mixture is hazardous.
- (ii) If a mixture has not been tested as a whole to determine whether the mixture is a health hazard, the mixture shall be assumed to present the same health hazards as do the components which comprise one percent (or, in the case of carcinogens, less than 0.1 percent) of the mixture, except that the mixture shall be assumed to present a health hazard if it contains a component known to be a carcinogen in a concentration of greater than 0.1 percent or greater than 1 percent, or greater

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(4) Written hazard communication program. (1) Employers shall develop, implement, and maintain at the work place, a written hazard communication program for their workplaces which at least describes how the criteria specified in paragraphs (f), (g), and (h) of this section for labels and other forms of warning, material safety data sheets, and employee information and training will be met, and which also includes the following:

- (i) A list of the hazardous chemicals known to be present using an identity that is referenced on the appropriate material safety data sheet (the list may be compiled for the workplace as a whole or for individual work areas); and
- (ii) The methods the employer will use to inform employees of the hazards of non-routine tasks (for example, the

cleaning of reactor vessels), and the hazards associated with chemicals contained in unlabeled pipes in their work areas.

(2) Multi-employer workplaces. Employers who produce, use, or store hazardous chemicals at a workplace in such a way that the employees of other employers may be exposed (for example, employees of a construction contractor working on site) shall additionally ensure that the hazard communication programs developed and implemented under this paragraph (e) include the following:

- (i) The methods the employer will use to provide the material safety data sheet, or to make it available at a central location in the workplace, for each hazardous chemical, the other employer(s) employees may be exposed to, while working;
- (ii) The methods the employer will use to inform the employer(s) of any precautionary measures that need to be taken to protect employees during the workplace's normal operating conditions and in foreseeable emergencies; and
- (iii) The methods the employer will use to inform the other employer(s) of the labeling system used in the work place.

(3) The employer may rely on an existing hazard communication program to comply with these requirements, provided that it meets the criteria established in this paragraph (e).

(4) The employer shall make the written hazard communication program available, upon request, to employees, their designated representatives, the Assistant Secretary and the Director, in accordance with the requirements of 29 CFR 1910.20(e).

(5) Labels and other forms of warning. (1) The chemical manufacturer, importer, or distributor shall ensure that each container of hazardous chemicals leaving the workplace is labeled, tagged or marked with the following information:

- (i) Identity of the hazardous chemical(s);
- (ii) Appropriate hazard warnings; and
- (iii) Name and address of the manufacturer or other responsible party.

(2) The methods the employer will use to inform employees of the hazards of non-routine tasks (for example, the

cleaning of reactor vessels), and the hazards associated with chemicals contained in unlabeled pipes in their work areas.

(2) Multi-employer workplaces. Employers who produce, use, or store hazardous chemicals at a workplace in such a way that the employees of other employers may be exposed (for example, employees of a construction contractor working on site) shall additionally ensure that the hazard communication programs developed and implemented under this paragraph (e) include the following:

- (i) The methods the employer will use to provide the material safety data sheet, or to make it available at a central location in the workplace, for each hazardous chemical, the other employer(s) employees may be exposed to, while working;
- (ii) The methods the employer will use to inform the employer(s) of any precautionary measures that need to be taken to protect employees during the workplace's normal operating conditions and in foreseeable emergencies; and
- (iii) The methods the employer will use to inform the other employer(s) of the labeling system used in the work place.

(3) The employer may rely on an existing hazard communication program to comply with these requirements, provided that it meets the criteria established in this paragraph (e).

(4) The employer shall make the written hazard communication program available, upon request, to employees, their designated representatives, the Assistant Secretary and the Director, in accordance with the requirements of 29 CFR 1910.20(e).

(5) Labels and other forms of warning. (1) The chemical manufacturer, importer, or distributor shall ensure that each container of hazardous chemicals leaving the workplace is labeled, tagged or marked with the following information:

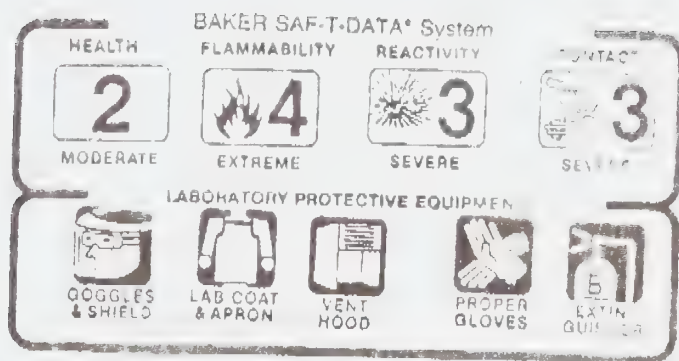
- (i) Identity of the hazardous chemical(s);
- (ii) Appropriate hazard warnings; and
- (iii) Name and address of the manufacturer or other responsible party.









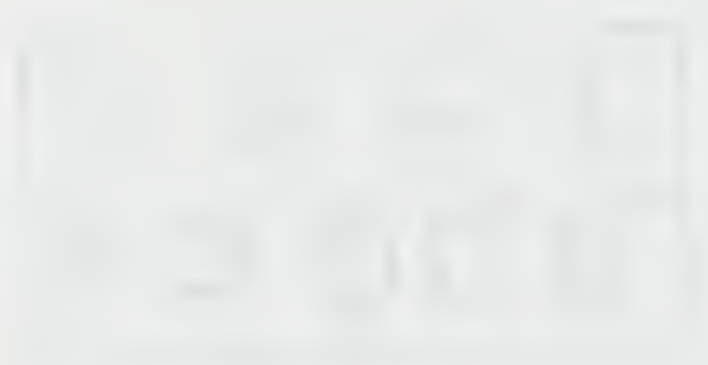


Graphic symbol labeling for Benzoyl Peroxide\*

Note the explosive symbol positioned under the "REACTIVITY"

\*From the 1. Baker, ... label







**AMERICA**

*The Great Indoors*

**91/92**

*Catalog*



**AMERICA**

*The Great Indoors*

**91/92**

**800-423-8610**





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MAY 15  
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1881



## RETURN SHIPMENTS

The customer shall please inspect the materials delivered for damage, defect or shortage immediately upon receipt and provide us notice of any such damage, defect or shortage within 30 days of receipt. All claims for any cause whatsoever, whether based on contract, negligence or other tort, strict liability, breach of warranty or otherwise shall be deemed waived unless we receive written notice of such claims no later than 30 days after your receipt of the materials as to which claim is made.

Defective or nonconforming materials shall be replaced by us without additional charge, or at our option by refund of the purchase price upon return of the materials. If it is necessary to return material, you must contact us for authorization and forwarding instructions.

Charges will be imposed on catalog items returned due to your error.

Orders under \$20.00: will not be authorized for return.

Orders over \$20.00: a minimum restocking charge of 20% will be imposed.

Additional charges may be made for returns or cancellations of special orders. Our liability for any and all claims, losses or damages arising from any cause, including our negligence shall in no event exceed the purchase price of the materials in respect to which the cause arose. In no event shall we be liable for incidental or consequential damages.

## PURITY

High purity is a requirement for every TCI product. All the chemicals listed in our catalog have been rigorously tested in our Quality Control Laboratory, for determination of purity and consistency. The purity and physical constants stated with the product listing are typical values and may vary slightly from lot to lot. If additional information is needed regarding purity, please contact our Technical Services Department.

## HAZARDOUS CHEMICALS

All of our chemicals should be handled only by qualified individuals familiar with their potential hazards and trained in proper laboratory procedures. Some chemicals are extremely toxic or otherwise hazardous. MSDS's will be provided as required by OSHA's Hazard Communication standard. The absence of a warning must not be interpreted as an indication of safety.

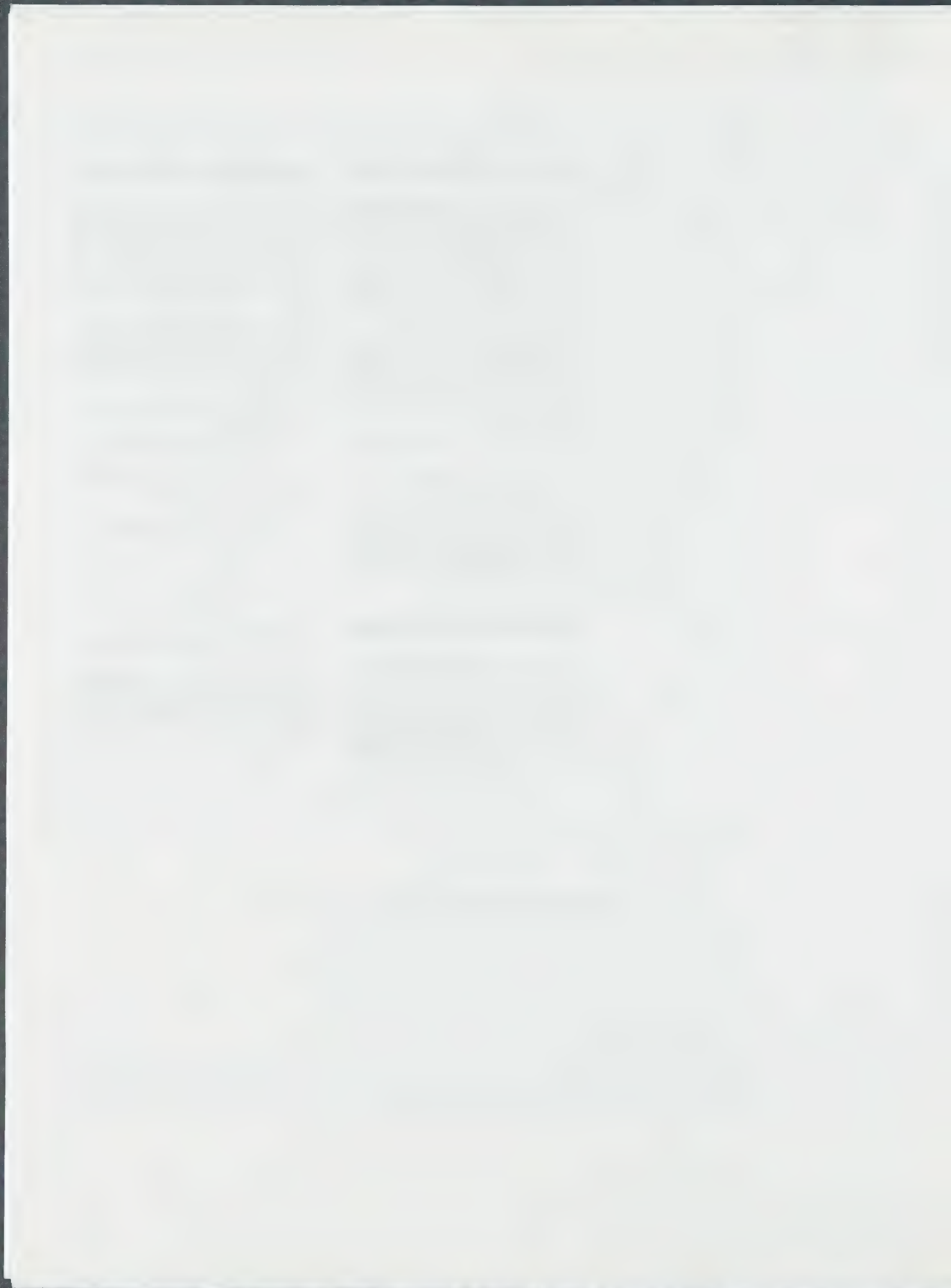
If a product is hazardous, the product description will carry a number of 1-9. This number is for one of the nine classes determined by the UN Committee of Experts on the Transport of Dangerous Goods. The UN classes relate to the type of hazard.

- 1 Explosives
- 2 Gases, compressed, liquefied, dissolved under pressure
- 3 Flammable liquids
- 4 Flammable solids, spontaneously combustible substances, water reactive substances
- 5 Oxidizing substances, organic peroxides
- 6 Toxic substances
- 7 Radioactive substances
- 8 Corrosives
- 9 Miscellaneous dangerous substances

## MATERIAL SAFETY

## DATA SHEETS MSDS

We supply MSDS's to our customers with the delivery of our product as required by the OSHA Hazard Communication Standard and many state laws. MSDS's are also available to customers for previously purchased products upon request.



M0558 Methylhydrazine (cis and trans isomers) 25 ml 19.95

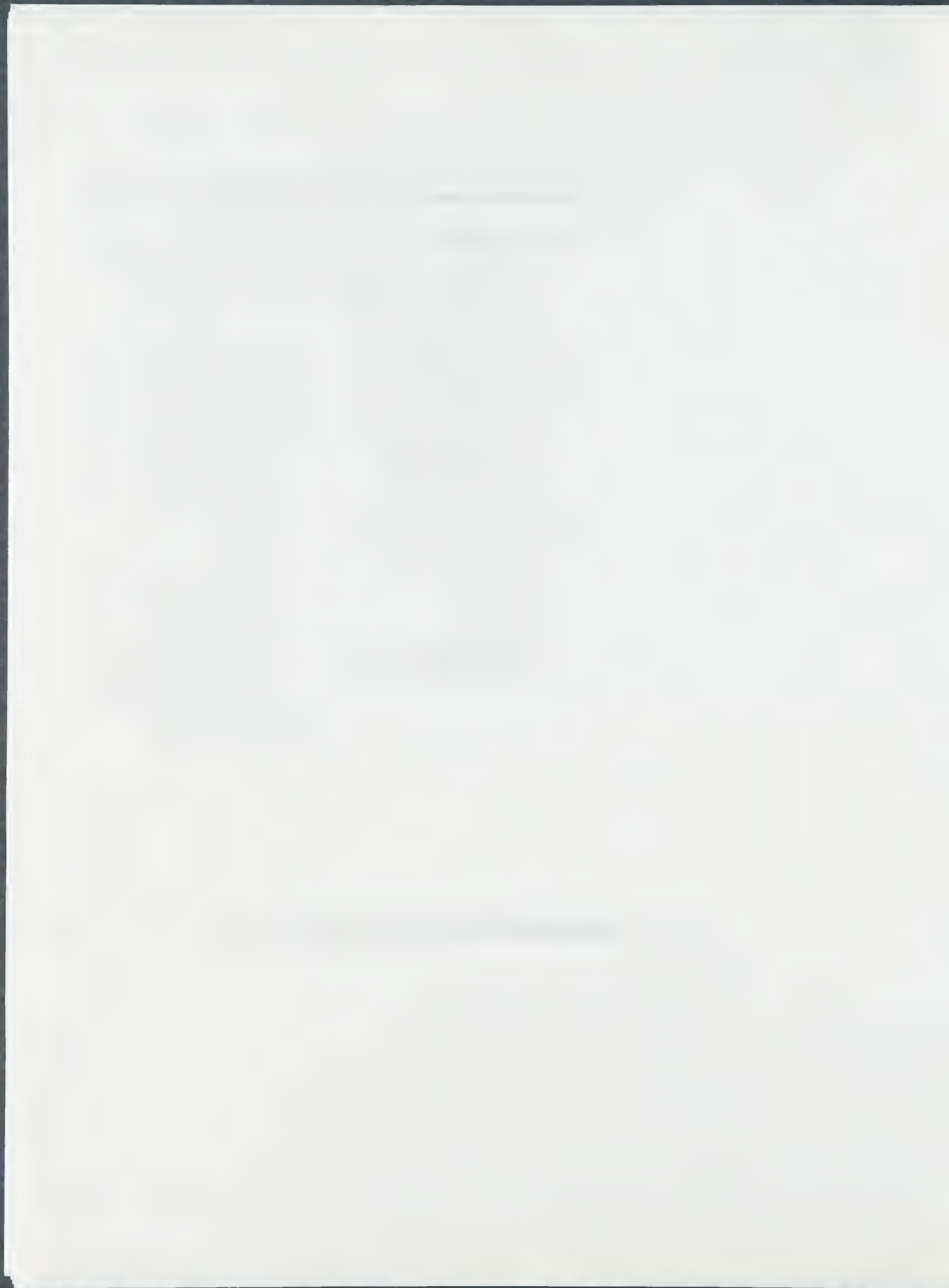
HN.NHCH<sub>3</sub> = 46.07 bp 87°C [lit.] RL 75 Re 421957 Merck 115957

eser 4.340 RTECS# MV56000000 HZ 3 FLAMMABLE LIQUID 160-34-4

TSCA

- 1 Order number of the chemical. Please use the order number with the code name when inquiring and ordering.
- 2 Name as described following chemical name is typical one only for reference.
- 3 Assay and analysis methods. Assay of different analysis methods.
- 4 Purity 99%(GC) by Gas Chromatograph analysis. 99% by Titrimetric Analysis. 99.99% by Gravimetric Analysis. No chemicals are tested in accordance with Japanese standards of JIS (Japanese Industrial Standards).
- 5 Quantity
- 6 Price
- 7 Molecular Formula or Linear Structural Formula. Molecular Weight. Water of Hydration. Density.
- 8 CAS No. (N<sub>2</sub>O<sub>2</sub>H<sub>2</sub>N<sub>2</sub>) = 394-47-1 (Anhydrous)
- 9 Technical Information
  - 9.1 Boiling Point (°C)
  - 9.2 Melting Point (°C)
  - 9.3 Flash Point (°C)
  - 9.4 Density
 This information is from literature and is not necessarily product specification.
- 10 Berlin volume (supplement) and page. For Berlin's Handbuch der Organischen Chemie, by Berlin Institute, Springer Verlag.
- 11 Monograph Number from The Merck Index (11th Edition, Merck & Co., Inc., U.S.A.).
- 12 CI Number from Colour Index (3rd Edition, The Society of Dyers and Colourists, England).
- 13 Hoeser & Prieser volume and page. Hoeser & Prieser Organic Synthesis, by Hoeser & M. Prieser, John Wiley & Sons, U.S.A.
- 14 RTECS number. From "Registry of Toxic Effects of Chemical Substances" (National Institute for Occupational Safety and Health, U.S.A.).
- 15 HZ - Hazardous class Number
  - 1. Explosive
  - 2. Gases, Compressed, Liquefied or Dissolved
  - 3. Flammable Gases
  - 4. Flammable Solids, Spontaneously Combustible Substances, Water reactive substance
  - 5. Oxidizing Substances, Organic Peroxide
  - 6. Poisonous (Toxic) Substances
  - 7. Radioactive substances
  - 8. Miscellaneous Dangerous Substances. The nine classes are determined by the UN Committee of Experts on the Transport of Dangerous Goods. The UN classes relate to the type of hazard.
- 16 UN Number
- 17 UN Name
- 18 Hazardous Material TSCA Inventory





1000	1,4-Dimethylpyridine 98% min	25g	1.00
	see 1,4-Xylydine	100g	4.00
1001	1,5-Dimethylpyridine 98% min	25g	1.00
	see 1,5-Xylydine	100g	4.00
1002	Dimethylpyridine mixture	25g	1.00
	see 1,4-Xylydine mixture	100g	4.00
1003	2,3-Dimethylpyridine Hydrochloride	25g	1.00
	see 2,3-Xylydine Hydrochloride	100g	4.00
1004	3-Dimethylpyridine Hydrochloride 98% min	25g	1.00
	see m-Xylydine Hydrochloride	100g	4.00
1005	4-Dimethylpyridine Hydrochloride 98% min	25g	1.00
	see p-Xylydine Hydrochloride	100g	4.00
1006	2,4-Dimethylpyridine-5-sulfonic Acid Sodium Salt	25g	1.00
	see m-Xylydine-5-sulfonic Acid Sodium Salt	100g	4.00
1007	2,4-Dimethylpyridine-6-sulfonic Acid Sodium Salt	25g	1.00
	see m-Xylydine-6-sulfonic Acid Sodium Salt	100g	4.00
1008	N,N-Dimethyl-m-aminopyridine 98% min	25g	1.00
	( $C_7H_{10}N_2$ ) FW 122.16 RTECS# A000000 HZ 6 Index (781-43-1)	100g	4.00
1009	N,N-Dimethylanthranic Acid Methylester	25g	1.00
	( $C_{10}H_{11}NO_3$ ) FW 197.20 RTECS# A000000 HZ 6	100g	4.00
1010	2,3-Dimethylsuccinonitrile	25g	1.00
	( $C_7H_{11}N_2$ ) FW 125.15 RTECS# A000000 HZ 6	100g	4.00
1011	Dimethyl Azodicarboxylate	25g	1.00
	see AZODICARBOXYLIC ACID Dimethyl Ester	100g	4.00
1012	3-Dimethylbenzoyl Acid 98% min	25g	1.00
	( $C_9H_{11}O_2$ ) FW 156.14 mp 129°C 740-42-61	100g	4.00
1013	N,N-Dimethylsuccinimide	25g	1.00
	( $C_7H_{11}NO$ ) FW 149.19 mp 59°C RTECS# CV4500000	100g	4.00
1014	1,3-Dimethylpyrrolidone	25g	1.00
	( $C_5H_9NO$ ) FW 111.13 mp 24°C	100g	4.00
1015	1,4-Dimethylpiperazine	25g	1.00
	( $C_6H_{12}N_2$ ) FW 112.17 mp 156°C	100g	4.00







Dr. Alfred Bader  
924 East Juneau, Suite 622  
Milwaukee, Wisconsin 53202  
Phone: 414/277-0730  
Fax: 414/277-0709

*A Chemist Helping Chemists*

February 22, 1996

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

As you will be able to imagine, I have been trying to think of the right expert in the field of explosives but have not been able to find such a person.

Regarding an expert in government regulations generally, one logical person is Dr. Ike Klundt, who retired from Aldrich some years ago after being a vice president in the company for many years. He is now partially retired, living in Colorado, and I understand from Tokyo Kasei that you are in touch with him. That is certainly a good decision.

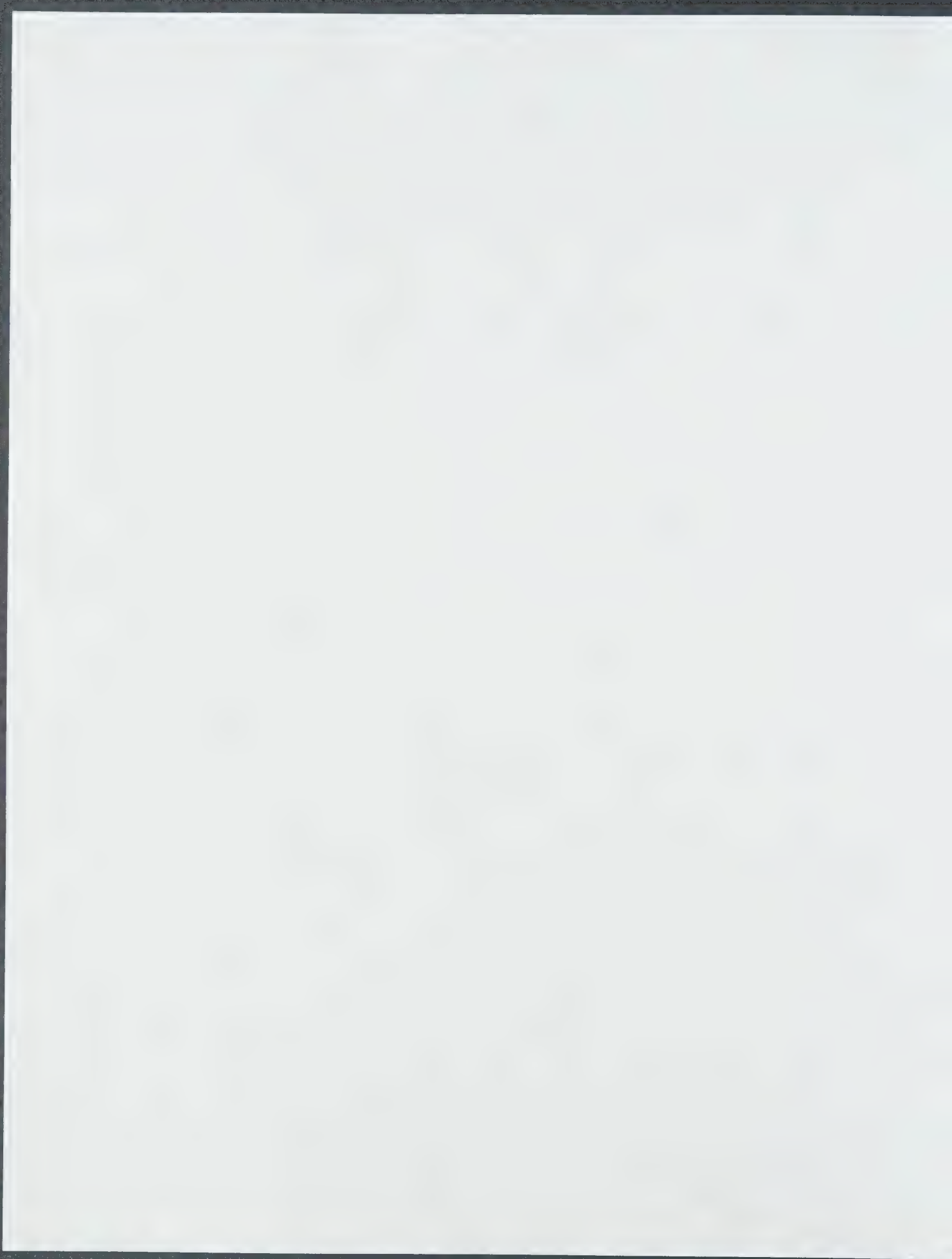
I enclose a copy of my invoice for consulting, which must have been overlooked.

With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosure





Dr. Alfred Bader  
924 East Juneau, Suite 622  
Milwaukee, Wisconsin 53202  
Phone: 414/277-0730  
Fax: 414/277-0709

*A Chemist Helping Chemists*

November 7, 1995

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

Please don't mind that I am responding to your letter of September 22nd only today, but you sent it to Bexhill-on-Sea, from where it was forwarded to us here in Milwaukee. We will be in Bexhill from November 13th through December 24th, but until next Monday, we are in Milwaukee.

As I had not heard from you in response to my letter of August 17th and the invoice enclosed therewith, I feared that you might somehow not be satisfied with the help I tried to give. But perhaps my letter and invoice got lost in the mails, and so I enclose copies.

By now, you might have finished reading my book. If you have read chapters 7, 12 and 13, you will realize how the culture at Aldrich and Sigma-Aldrich has changed over the years. I always tried to help all chemists, whether customers, suppliers or competitors, but that unfortunately is no longer so.

Aldrich would not allow Bob Langa to consult for Tokyo Kazai, and I am afraid that I do not know of experts elsewhere either in OSHA matters or with explosives.

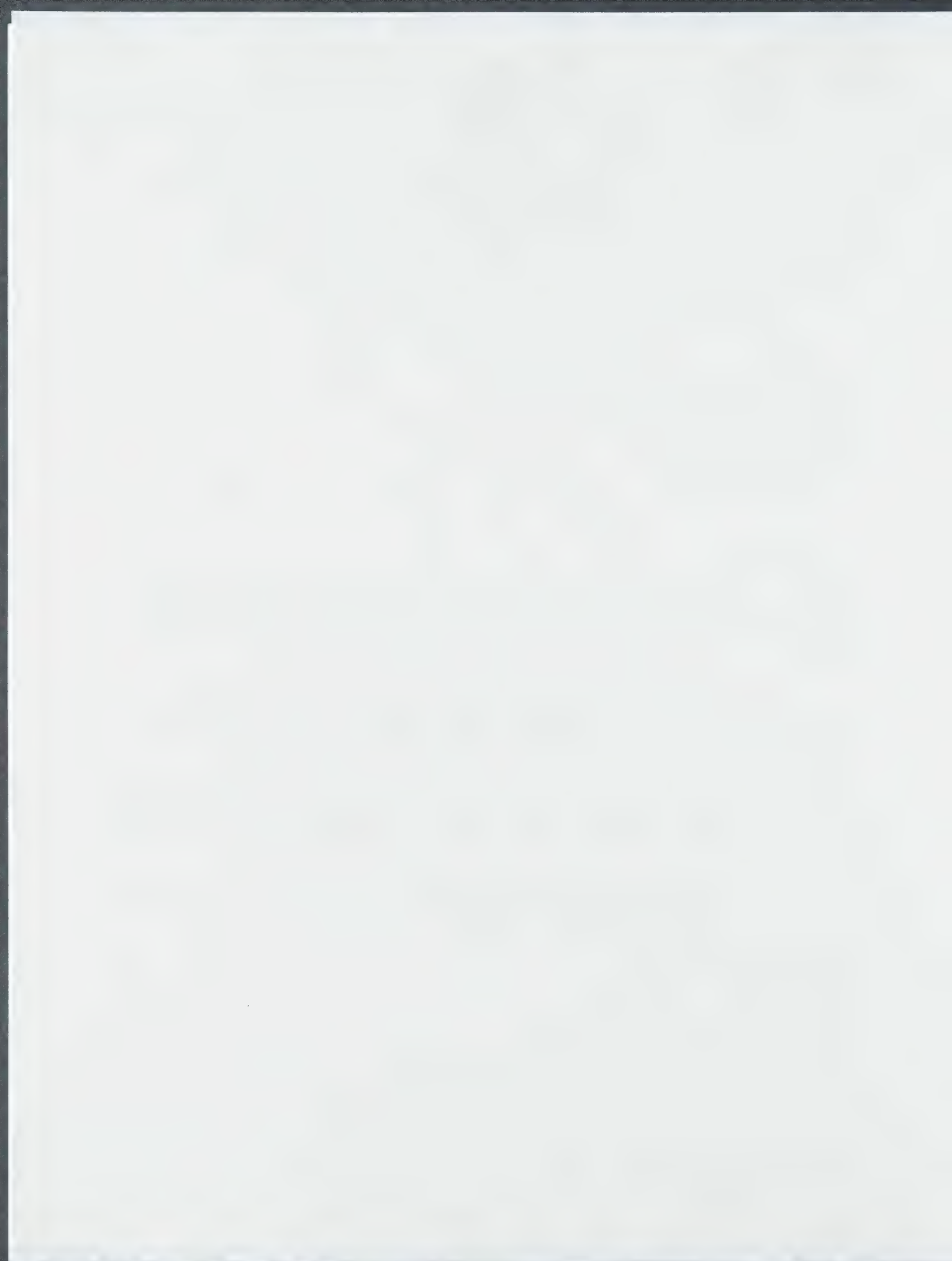
With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosures





# HINSHAW & CULBERTSON

CHICAGO, ILLINOIS  
BELLEVILLE, ILLINOIS  
BLOOMINGTON, ILLINOIS  
CHAMPAIGN, ILLINOIS  
JOLIET, ILLINOIS  
LISLE, ILLINOIS  
PEORIA, ILLINOIS  
SPRINGFIELD, ILLINOIS

220 EAST STATE STREET  
P. O. BOX 1389  
ROCKFORD, ILLINOIS 61105-1389

815.963.8488

TELEFAX 815.965.9529

WAUKEGAN, ILLINOIS  
FT. LAUDERDALE, FLORIDA  
MIAMI, FLORIDA  
TAMPA, FLORIDA  
ST. LOUIS, MISSOURI  
APPLETON, WISCONSIN  
BROOKFIELD, WISCONSIN  
MILWAUKEE, WISCONSIN

September 22, 1995

FILE NO.  
726608


Dr. Alfred R. Bader  
52 Wickham Avenue  
Bexhill-on-Sea  
East Sussex, TN39 3ER

Dear Dr. Bader:

As a follow-up to our recent meeting, I wondered if you had any progress with some of the items we discussed. In particular, have you had an opportunity to determine whether Bob Langa would be in a position to, and willing to, consult with us concerning the issues in this case, particularly concerning compliance with various OSHA requirements. Also, have you had an opportunity to consider and recommend to us, a chemist with credentials that would qualify him to testify in court as to the various scientific issues we discussed as being pertinent in this case? Although we have no deadline at this time, I know that the court will give us a deadline soon. I would be grateful if you would look into this at your earliest convenience.

Thank you for your assistance.

Very truly yours,

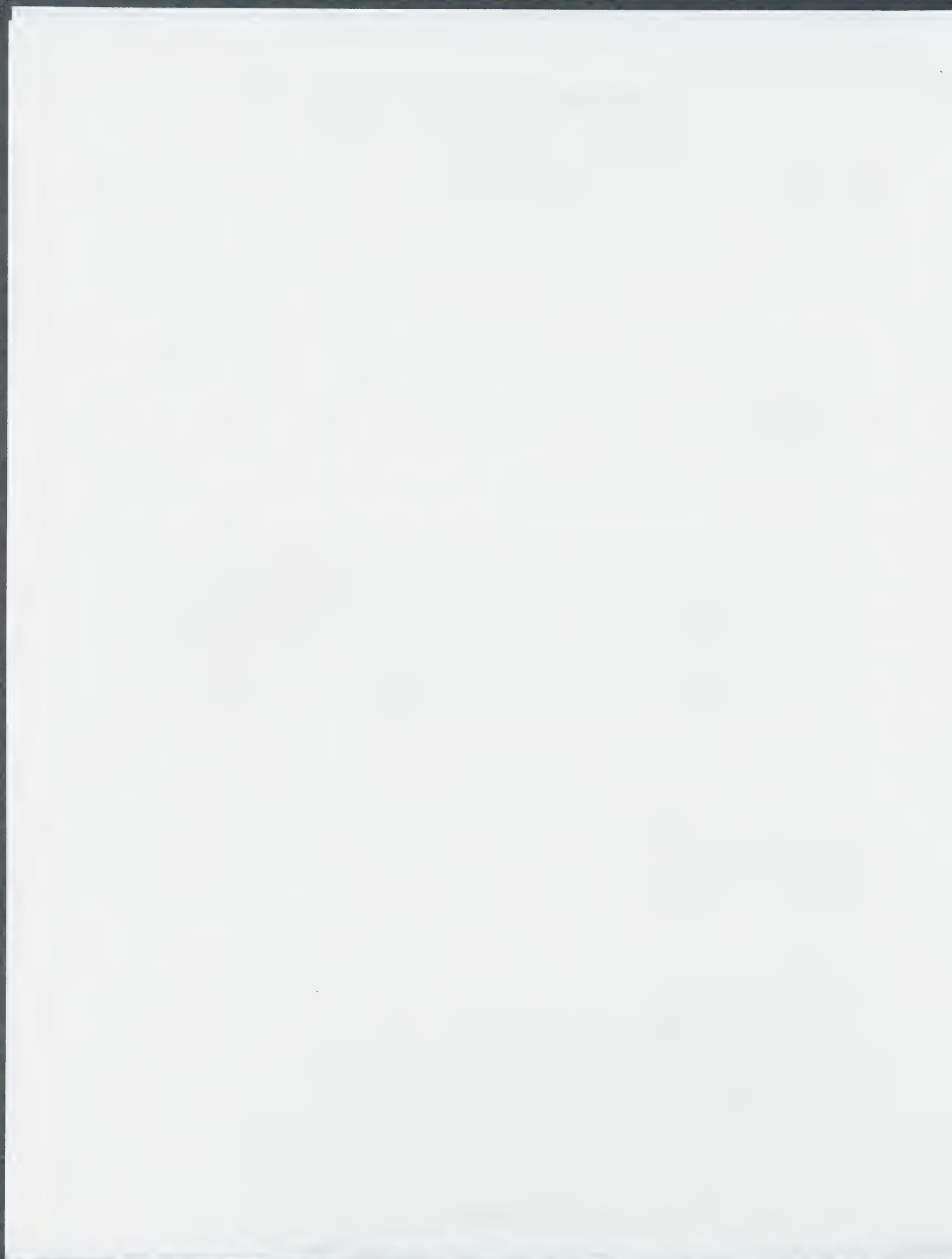
  
THOMAS H. BOSWELL  
For Hinshaw & Culbertson

THB:jls

cc: Mr. Masa Isono  
Mr. Ronald Ragen  
Mr. John Langhenry

P.S. I have started reading your book. It is most fascinating.

c:\data\thb\726608\co\bader.002





Dr. Alfred Bader  
2961 North Shepard Avenue  
Milwaukee, Wisconsin 53211

*A Chemist Helping Chemists*

August 17, 1995

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

Dear Mr. Boswell:

I really enjoyed meeting you today. I hope that my discussion and also yours with Bob Lenga were helpful to you.

I think the three most important points coming from our discussion are:

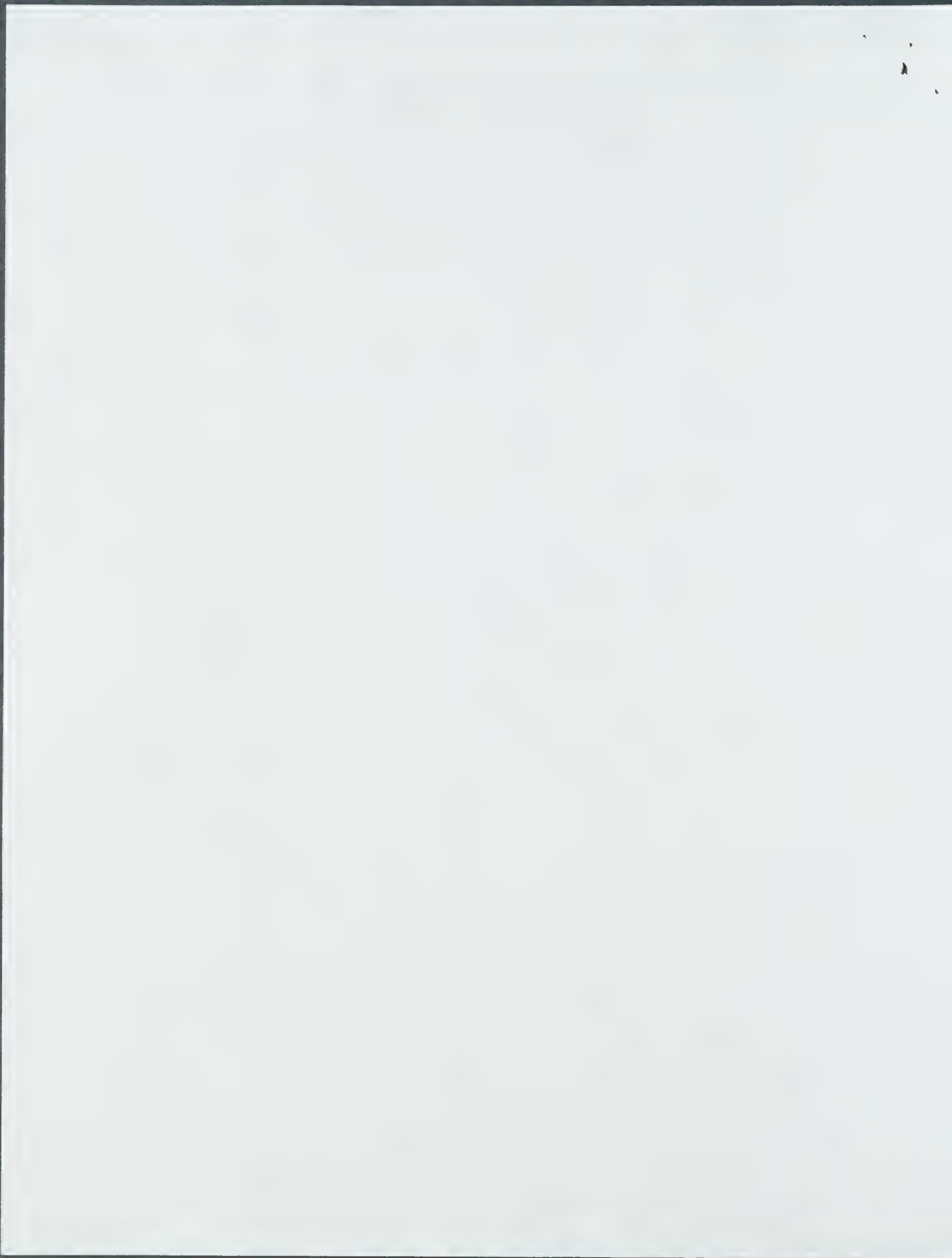
- 1) that there were at least three other hazardous chemicals thrown away at the same time, namely benzyl chloroformate, hydrazine hydrate and propiolic acid;
- 2) Dr. Jay Young included a serious mistranslation of the original German paper. There is a world of difference between a compound "going pop" and exploding; and
- 3) that the preparation of dimethyl azodicarboxylate is described in detail in a standard text, Organic Syntheses, which describes the preparations of many common and widely used reagents. Only in a warning dated June 1995 did Organic Syntheses point out that dimethyl azodicarboxylate can explode on heating.

We agreed that I would bill you \$100.00 per hour for consulting, but only for solid hours of work. I hope that you will call me or fax me from time to time to tell me about developments, and of course, a few minutes' involvement on the phone or in my library will not be charged.

With all good wishes, I remain,

Yours sincerely,

AB/cw  
Enclosure - Invoice



Dr. Alfred Bader  
2961 North Shepard Avenue  
Milwaukee, Wisconsin 53211

*A Chemist Helping Chemists*

August 17, 1995

**INVOICE**

Thomas H. Boswell, Esq.  
Hinshaw & Culbertson  
220 East State Street  
P.O. Box 1389  
Rockford, IL 61105-1389

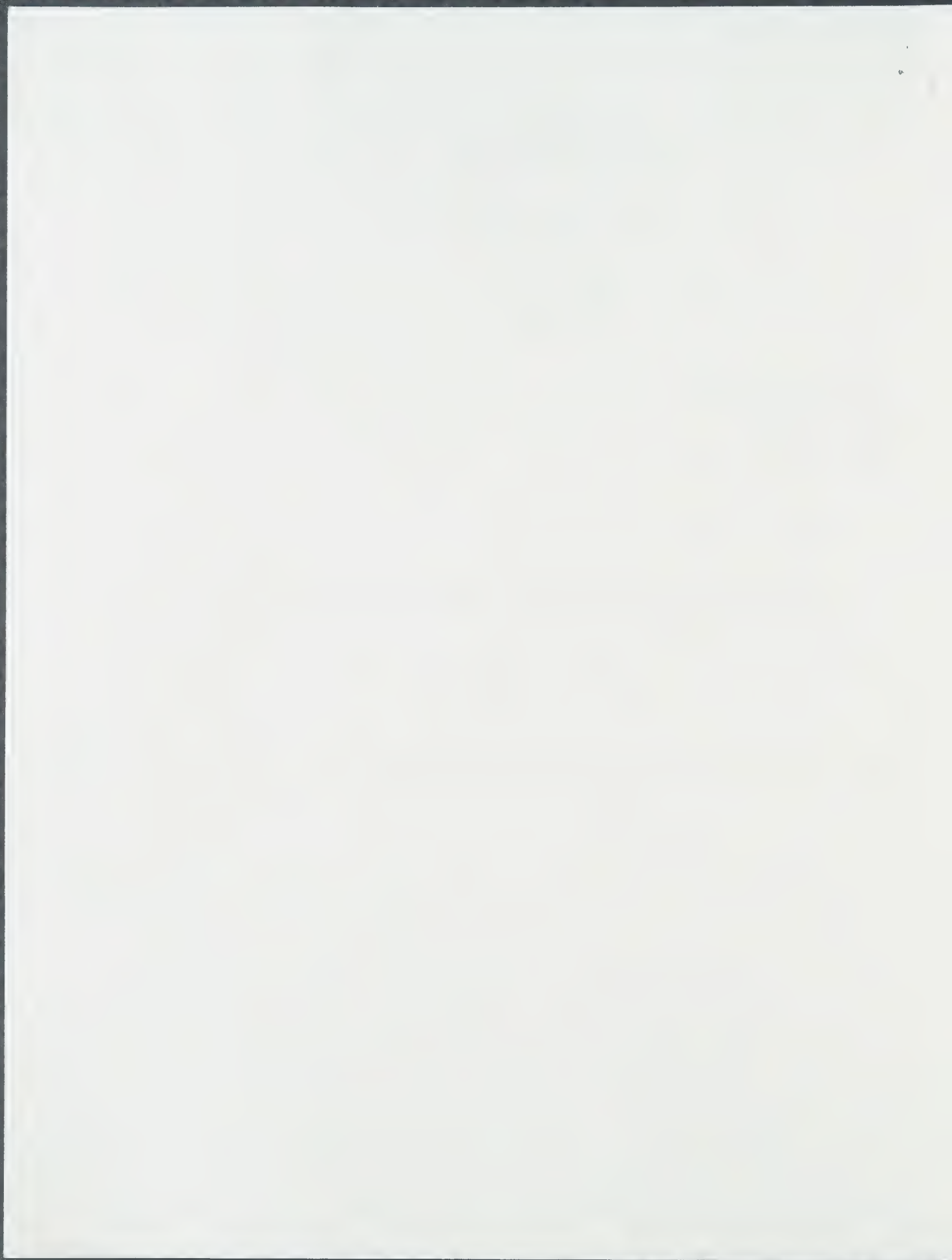
Your file no. 726608

For consultation re: the explosive nature of dimethyl azodicarboxylate,  
circa 5 hours at \$100.00/hour

**NET DUE: \$500.00**

NB: [REDACTED]





②

Popwell

Benzyl chloroformate  
hydrazine hydrate  
progesterone acid

---

with Hauslalom





STATE OF NEW YORK

IN SENATE

January 10, 1911.

REPORT

OF THE

COMMISSIONERS OF THE LAND OFFICE

IN ANSWER TO A RESOLUTION PASSED BY THE SENATE

APRIL 10, 1909.

ALBANY:

THE UNIVERSITY OF THE STATE OF NEW YORK PRESS,

1911.

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Will follow

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FAX FROM



DR. ALFRED R. BADER  
52 Wickham Avenue  
Bexhill-on-Sea  
East Sussex TN39 3ER  
Telephone/Fax: 40424-22-22-23

Phone 44-1424 210 684

Date: July 20 1995

Page 1 of 2

To:  
Fax:

Mr. Thomas Bopprell

Stephen E. Culbertson 001 815 965 4528

Re. Your file 726608

Dear Mr. Bopprell

I hope you will have spoken to Dr. Richard Pariza\*. I am returning to Milwaukee on July 24<sup>th</sup> and my calendar for the week following is reasonably free.

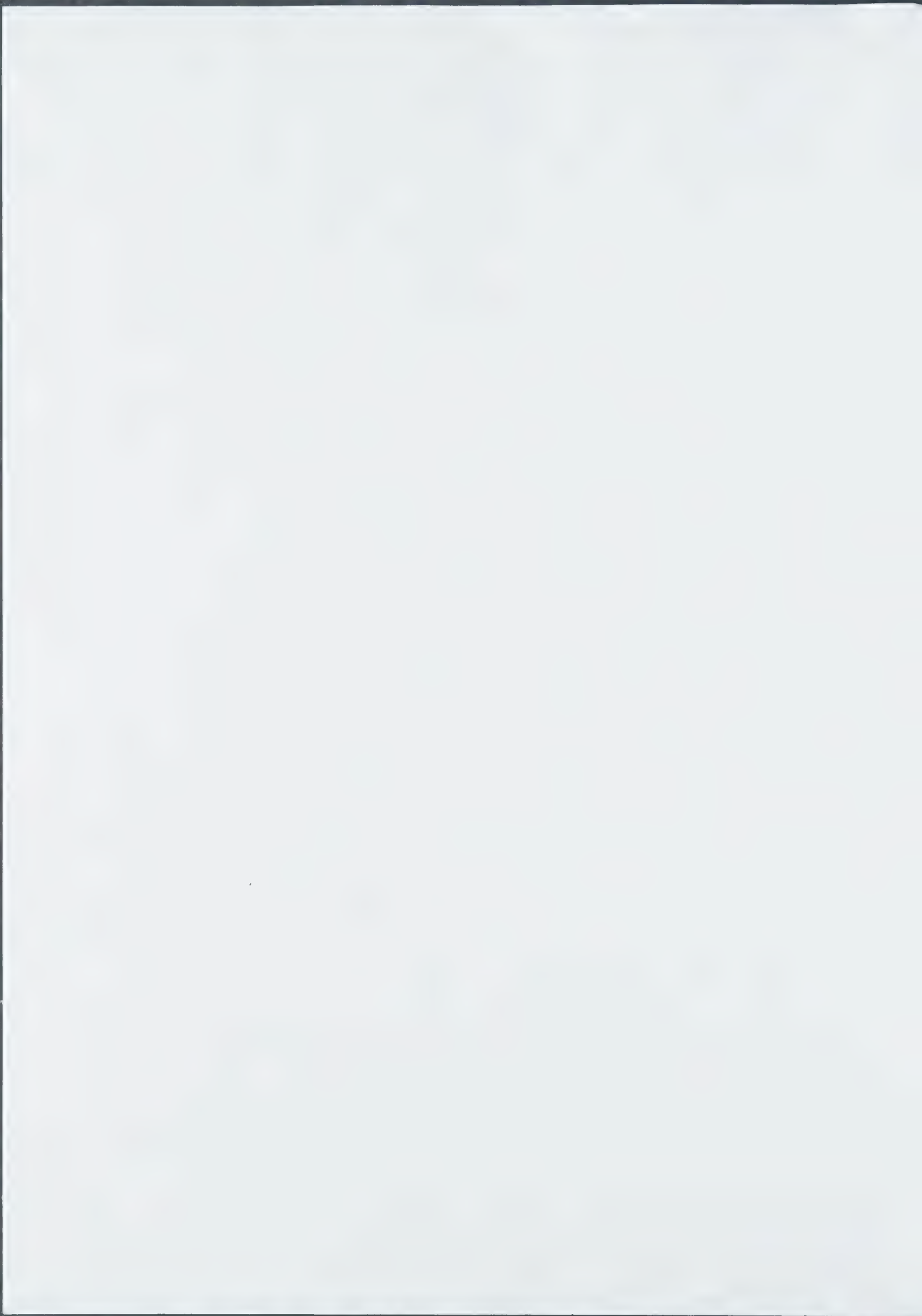
Attached is Aldrich's safety information on a related ester of azodicarbonyl<sub>2</sub> and. Note instructions to vent periodically & to refrigerate. The key questions: Did Pearce refrigerate (likely) and vent (unlikely) and how long did Pearce have the material?

Best wishes

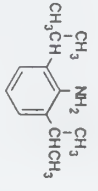
Alfred Bader

\* His phone is  
708 872 6925





2,6-Diisopropylaniline  
 CAS:124944-04-5  
 Aldrich 15,771-6



**APPEARANCE:**  
Brown liquid

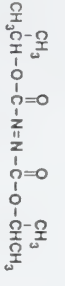
**RTCS# BX4025000**

**TOXICITY DATA:** oral LD50: 3204 mg/kg.

**HEALTH HAZARDS:** May be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes and upper respiratory tract. Causes skin irritation. Absorption into the body leads to the formation of methemoglobin which in sufficient concentration causes cyanosis. Onset may be delayed 2 to 4 hours or longer.

mp: 45°  
 bp: 257°  
 Fp: 255°F(123°C)  
 Fw: 177.29  
 d: 0.940  
 nD: 1.5392

Diisopropyl azodicarboxylate  
 CAS:12446-83-5  
 Aldrich 22,554-1



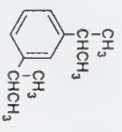
**APPEARANCE:**  
Orange liquid

**TOXICITY DATA:**  
To the best of our knowledge, the toxicological properties have not been thoroughly investigated.

**HEALTH HAZARDS:** May be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes and upper respiratory tract. Causes skin irritation.

bp: 75°/0.25mm  
 Fp: 223°F(106°C)  
 Fw: 202.21  
 d: 1.027  
 nD: 1.4205

1,3-Diisopropylbenzene  
 CAS:99-62-7  
 Aldrich 11,326-3



**APPEARANCE:**  
Colorless liquid

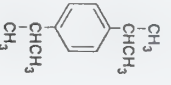
**RTCS# CZ6334000**

**TOXICITY DATA:** oral LD50: 7400 mg/kg.

**HEALTH HAZARDS:** May be harmful by inhalation, ingestion, or skin absorption. May cause eye irritation. May cause skin irritation.

mp: -63°  
 bp: 203°  
 Fp: 170°F(76°C)  
 Fw: 162.28  
 d: 0.856  
 nD: 1.4890

1,4-Diisopropylbenzene  
 CAS:100-18-5  
 Aldrich 12,627-6



**APPEARANCE:**  
Colorless liquid

**RTCS# CZ6360000**

**TOXICITY DATA:** oral LD50: 3400 mg/kg.

**HEALTH HAZARDS:** May be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes and upper respiratory tract. Causes skin irritation.

bp: 203°  
 Fp: 170°F(76°C)

**FIRST AID:** In case of contact, immediately flush eyes or skin with copious amounts of water for at least 15 minutes while removing contaminated clothing and shoes. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. If ingested, wash out mouth with water. Call a physician. Wash contaminated clothing before reuse.

**INCOMPATIBILITY:** Acids, acid chlorides, acid anhydrides, chloroformates and strong oxidizing agents.

**DECOMPOSITION PRODUCTS:** Toxic fumes of: carbon monoxide, carbon dioxide and nitrogen oxides.

**HANDLING AND STORAGE:** Wear appropriate NIOSH/MSHA-approved respirator, chemical-resistant gloves, safety goggles, other protective clothing. Safety shower and eye bath. Mechanical exhaust required. Do not breathe vapor. Avoid contact with eyes, skin and clothing. Readily absorbed through skin. Wash thoroughly after handling. Irritant. Harmful liquid. Keep tightly closed. Store in a cool dry place.

**WASTE DISPOSAL:** 2  
**SPILLS OR LEAKS:** d,l,a,f  
**EXTINGUISHING MEDIA:** C,G

**FIRST AID:** In case of contact, immediately flush eyes with copious amounts of water for at least 15 minutes. In case of contact, immediately wash skin with soap and copious amounts of water. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. If ingested, wash out mouth with water. Call a physician. Wash contaminated clothing before reuse.

**INCOMPATIBILITY:** Strong oxidizing agents, strong bases, alcohols. Store away from heat and direct sunlight. May discolor on exposure to light.

**DECOMPOSITION PRODUCTS:** Toxic fumes of: carbon monoxide, carbon dioxide and nitrogen oxides.

**HANDLING AND STORAGE:** Chemical safety goggles. NIOSH/MSHA - approved respirator. Use only in a chemical fume hood. Compatible chemical-resistant gloves. Safety shower and eye bath. Do not breathe vapor. Avoid contact with eyes, skin and clothing. Wash thoroughly after handling. Irritant. Keep container closed. Light-sensitive. May develop pressure. Vent periodically. Refrigerate.  
 Decomposes vigorously over 100 °C.

**WASTE DISPOSAL:** 2  
**SPILLS OR LEAKS:** l,k,l,f  
**EXTINGUISHING MEDIA:** C,G

**FIRST AID:** In case of contact, immediately flush eyes with copious amounts of water for at least 15 minutes. In case of contact, immediately wash skin with soap and copious amounts of water. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. If ingested, wash out mouth with water. Call a physician. Wash contaminated clothing before reuse.

**INCOMPATIBILITY:** Strong oxidizing agents.

**DECOMPOSITION PRODUCTS:** Toxic fumes of: carbon monoxide, carbon dioxide.

**HANDLING AND STORAGE:** Chemical safety goggles. Rubber gloves. NIOSH/MSHA - approved respirator. Safety shower and eye bath. Mechanical exhaust required. Do not breathe vapor. Do not get in eyes, on skin, on clothing. Wash thoroughly after handling. Keep tightly closed. Keep away from heat and open flame. Store in a cool dry place. Combustible.

**WASTE DISPOSAL:** 3  
**SPILLS OR LEAKS:** d,l,a,f  
**EXTINGUISHING MEDIA:** C,G

**FIRST AID:** In case of contact, immediately flush eyes with copious amounts of water for at least 15 minutes. In case of contact, immediately wash skin with soap and copious amounts of water. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. If ingested, wash out mouth with water. Call a physician. Wash contaminated clothing before reuse.

**HANDLING AND STORAGE:** Chemical safety goggles. Rubber gloves. NIOSH/MSHA - approved respirator. Safety shower and eye bath. Mechanical exhaust required. Do not breathe vapor. Do not get in eyes, on skin, on clothing. Wash thoroughly after handling. Irritant. Keep tightly closed. Keep away from heat and open flame. Store in a cool dry place. Combustible.

**WASTE DISPOSAL:** 3  
**SPILLS OR LEAKS:** d,l,a,f  
**EXTINGUISHING MEDIA:** C,G

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# HENSHAW & CLIBERTSON

## HELICOPTER TRANSMISSION

TO: [Faint recipient address]

FROM: [Faint sender address]

RE: [Faint subject line]

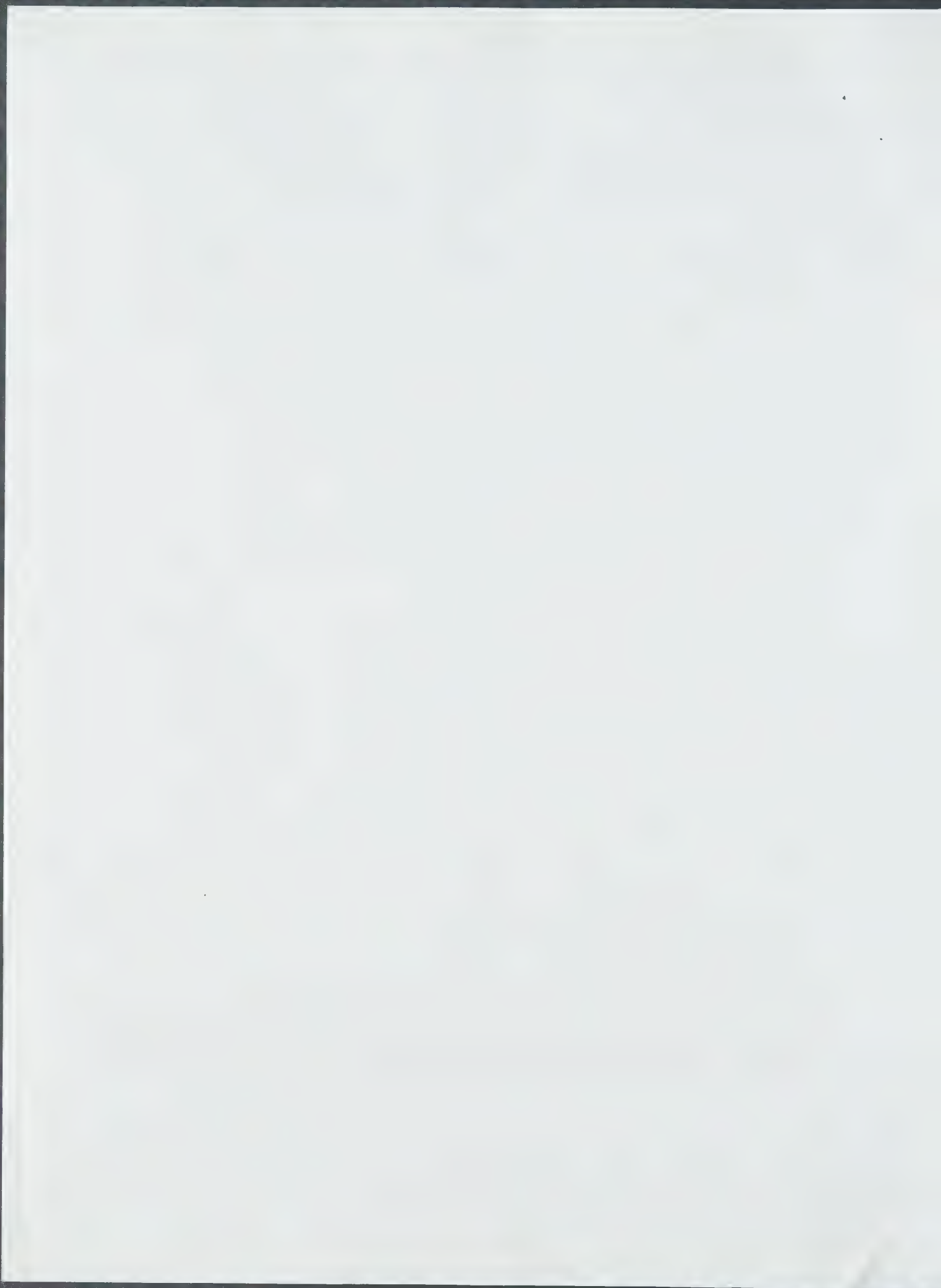
[Faint body text]

[Faint closing text]

IF YOU DO NOT RECEIVE THIS TRANSMISSION, PLEASE CALL  
IF YOU HAVE RECEIVED THIS FACSIMILE IN ERROR, PLEASE NOTIFY US BY TELEPHONE IMMEDIATELY AND RETURN THE TRANSMITTED DOCUMENT TO US AT THE ADDRESS ABOVE BY U.S. MAIL AT YOUR EXPENSE.

TERMINATED

[Faint footer text]





Jay A. Young, Ph.D.

10/1/85  
10/1/85  
10/1/85  
10/1/85

10/1/85  
10/1/85

URGENT TO YOUR REQUEST OF 10/1/85 RE: [unclear]

The chemical structure shown is a substituted benzene ring with various functional groups. It is a complex organic molecule, possibly a pharmaceutical intermediate or a specific chemical reagent. The structure includes a benzene ring with substituents at the 1, 2, 3, and 4 positions, including what appears to be a hydroxyl group, a methyl group, and other functional groups.

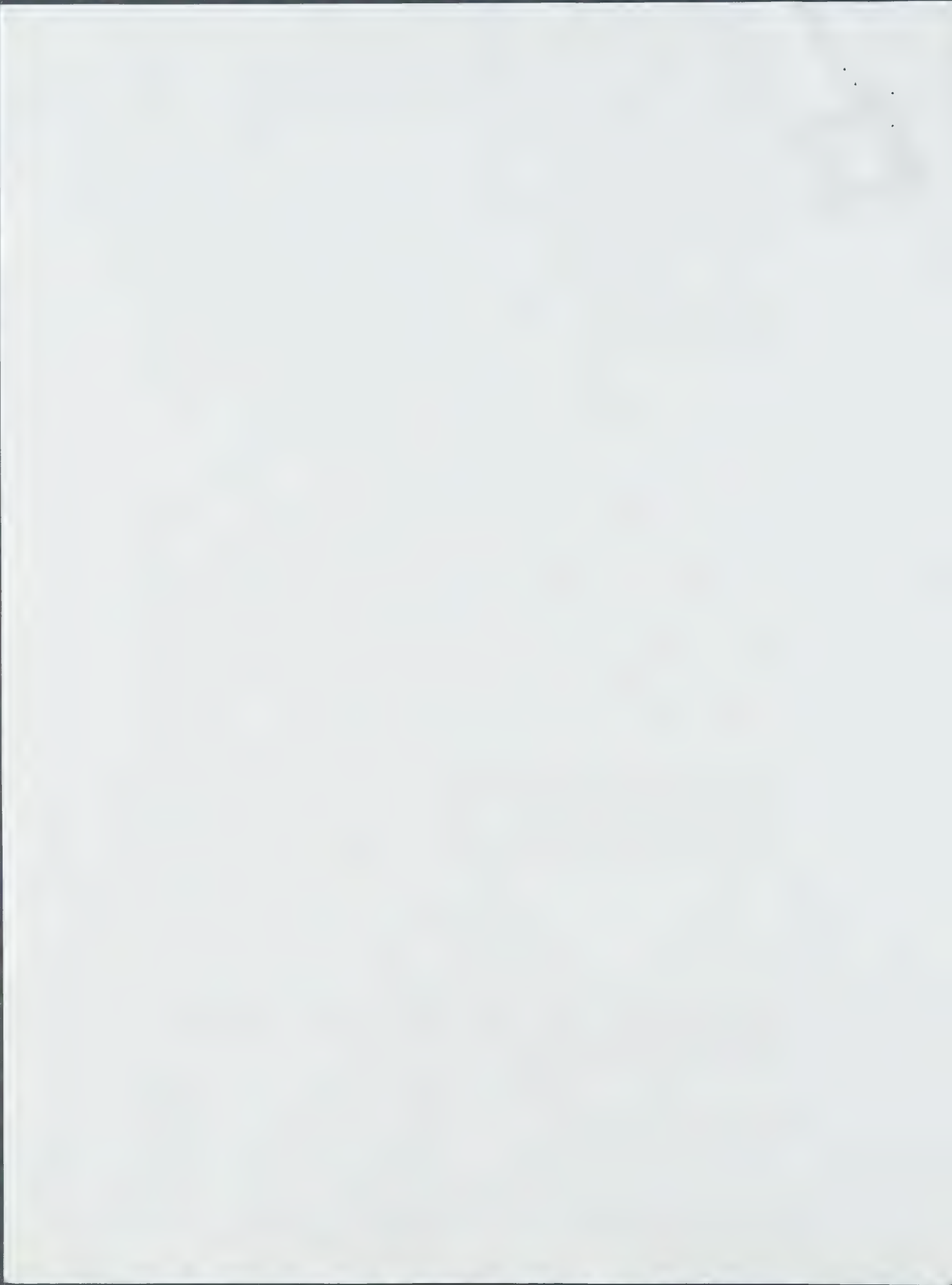
and the compound is a white solid with a melting point of approximately 150°C. It is soluble in water and ethanol. The compound is used in the synthesis of various pharmaceuticals and dyes. The following is a list of its properties:

When triggered, the resulting signal is a sharp peak with a half-width of about 100 ns. The signal is very stable and can be used for precise timing measurements.

10/1/85

10/1/85  
10/1/85  
10/1/85





that is, it is a low velocity, high density explosive.

On the other hand, many of the types used in the past also are used because of the way they are used. They are used in their new form for the same purpose as the original material. They are used in the same way as the original material.

NO

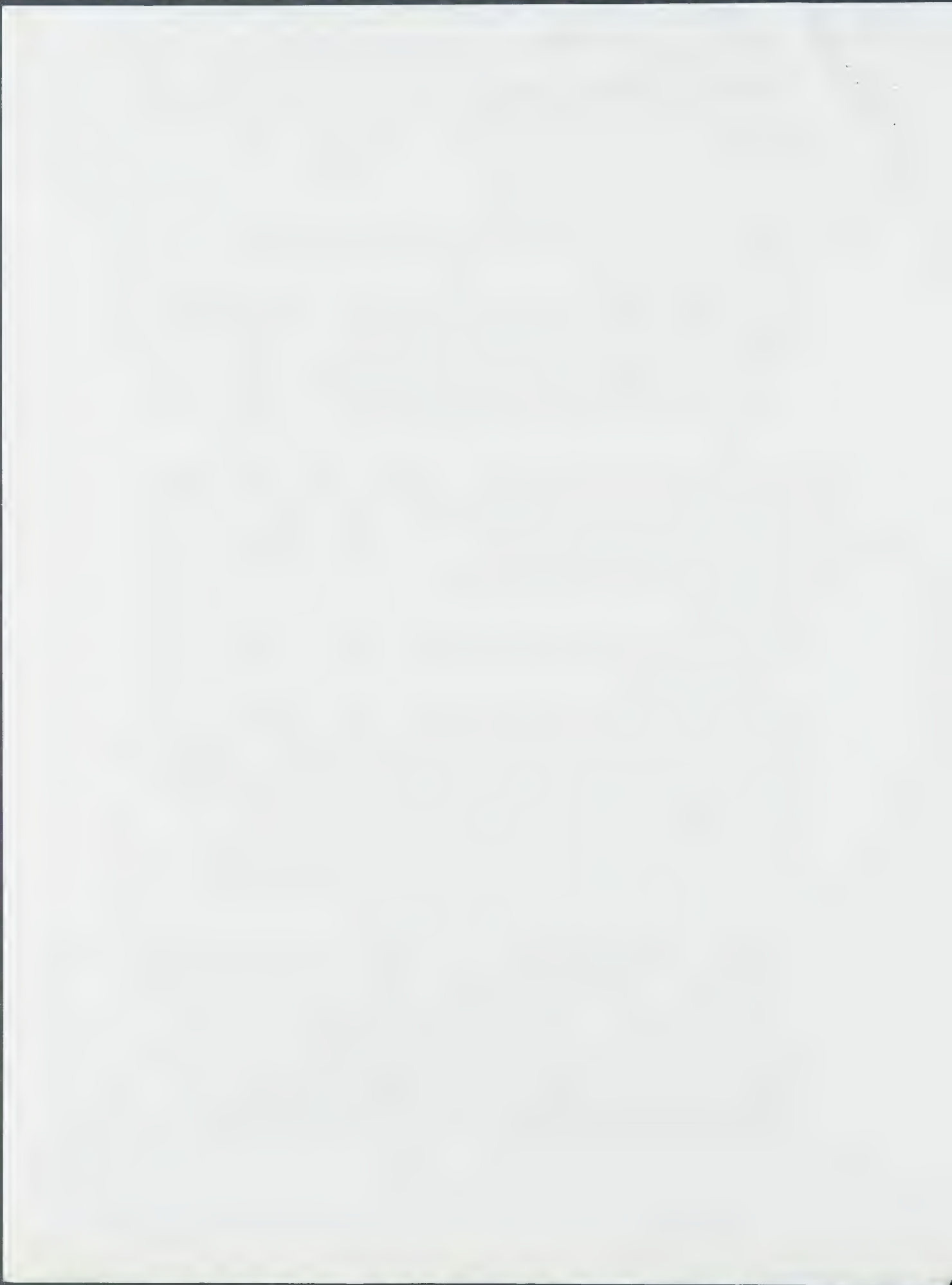
It has been known for some time that dimethyl azodicarboxylate is explosive. When it was first prepared and information about its properties was available, it was described as an explosive which "burns slowly" and "explodes like gunpowder" (translated from French and English). See also the abstract-translation "decomposes like gunpowder" (the abstract, July 1, 1957).

The pages from the above references and from other references cited below are attached to this report.

Dimethyl azodicarboxylate was described in an internationally well-known reference work, "Properties of Industrial Materials", Vol. 10, No. 11, (1957) as "shock sensitive, burns rapidly" (Sheldon Sheppard, et al. in United States Patent 2,814,855, issued October 17, 1957 describes dimethyl azodicarboxylate as "shock sensitive" and, further characterizes its impact sensitivity as 2 kg. 1 inch fall. Thus dimethyl azodicarboxylate is three and one-half times more sensitive to impact than nitrocellulose and four times more sensitive to impact than black powder.

Dimethyl azodicarboxylate is more explosive than black powder. When black powder is exploded, the volume increases by a factor of approximately 500. In the same volume the expansion in the products, compared to the factor of greater than 700 for dimethyl azodicarboxylate.

The above comparisons show that dimethyl azodicarboxylate would be a better explosive than black powder and approximately equal to smokeless powder (which is a derivative of gunpowder). But it should be used in place of these explosives because it is too unstable, too





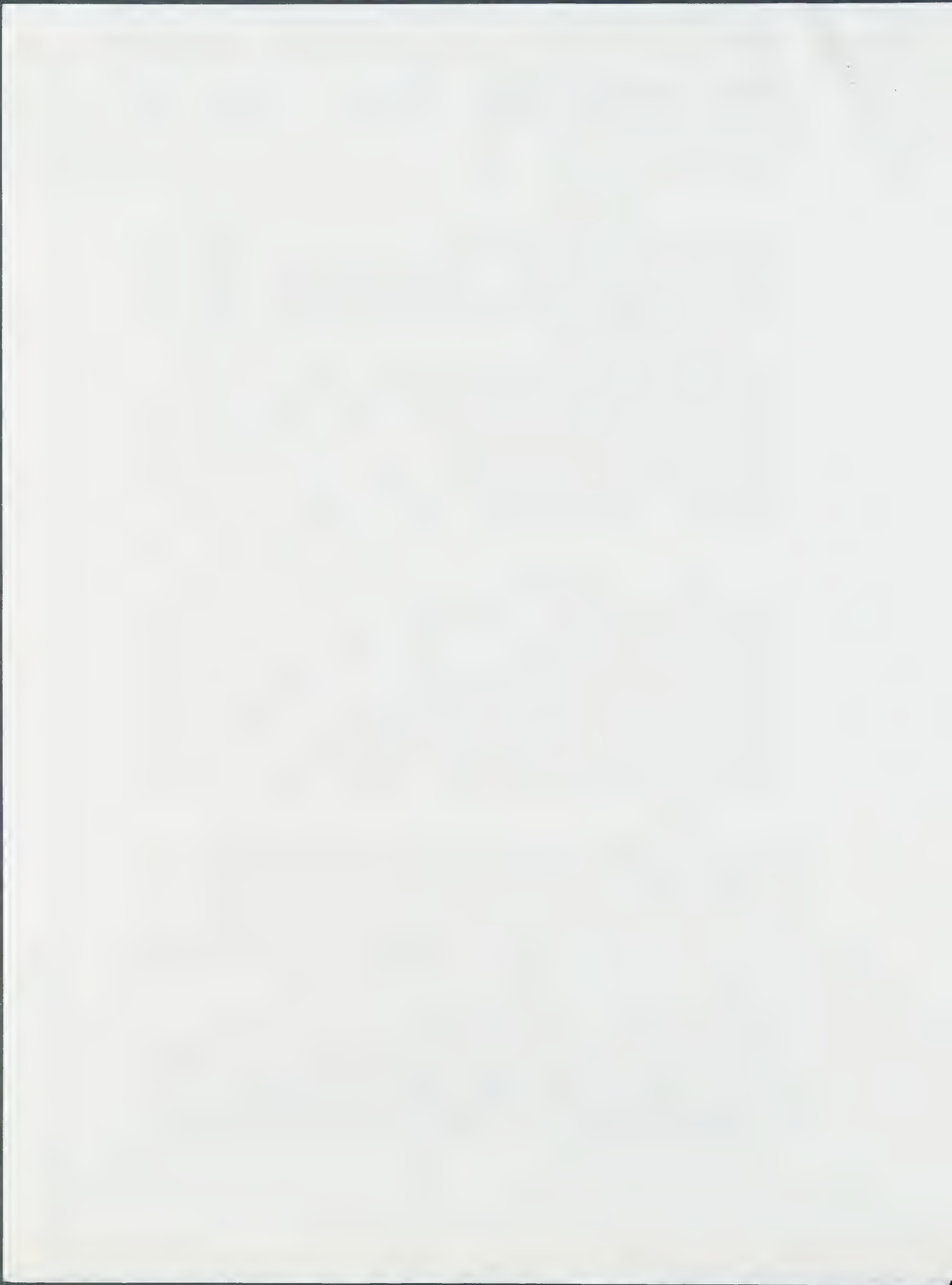
sensitive to shock or other disturbance. As it ages in storage it tends to become even more sensitive, more unpredictable. Although it is a very powerful explosive it is too dangerous, too much likely to explode before you want it to explode, to be a useful explosive.

The use for dimethyl azodicarboxylate is as a chemical research tool in the laboratory where one uses small amounts so that the laboratory equipment can withstand the force of an unexpected explosion. As an example, dimethyl azodicarboxylate is used in the synthesis of various compounds in which the reaction is highly exothermic. When the molecule is fully constructed, the material explodes, leaving fragments of the molecule as "free radicals". Free radicals are chemical species with properties that are useful in various laboratory applications.

When dimethyl azodicarboxylate is purchased for use in a laboratory the package from the supplier is handled by the people who take care of transportation of the material from the supplier to the laboratory. At the laboratory the package is opened and the chemical is handled and used by research laboratory technicians. If the material is not used or unused is handled by employees of the laboratory. Since the common practice in the operation of a research laboratory is to purchase a little more, rather than a little less, of the chemicals that are used, there is almost always some left over or unused chemical material.

While a hazardous chemical is inside of its original package, it poses little danger. Shipped packages are required to be specially labeled and packed according to shipping regulations. As long as employees involved in transportation of the package follow the applicable regulations, no problem is involved. When the material is received at the laboratory and the bottle is opened, the chemical is removed from its shipping container, it becomes a hazard that must be controlled.

Special procedures must be employed to use it safely. First, the laboratory workers must know what the hazards are, they must be warned. And second, they need to know the precautions to be followed when they use the hazardous chemical. When properly done, the labels on the container and the information in the Material Safety Data Sheet for the chemical provide this necessary safety information.



Similarly, the employees of the disposal contractor must rely on the labels and the material safety data sheet for safety information as they handle the hazardous chemical when they prepare it for disposal.

It is the foreseeable users and handlers of hazardous chemicals such as dimethyl azodicarboxylate are people who do the shipping, the laboratory workers, and the employees of disposal contractors. To handle dimethyl azodicarboxylate safely, they rely on the safety information on the labels and in the material safety data sheets. When a chemical is as dangerously explosive as dimethyl azodicarboxylate, it is foreseeable that without the necessary knowledge, foreseeable users and handlers could be severely injured or killed.

For the safe use of hazardous chemicals, it is foreseeable that labels and material safety data sheets provide the necessary warning information.

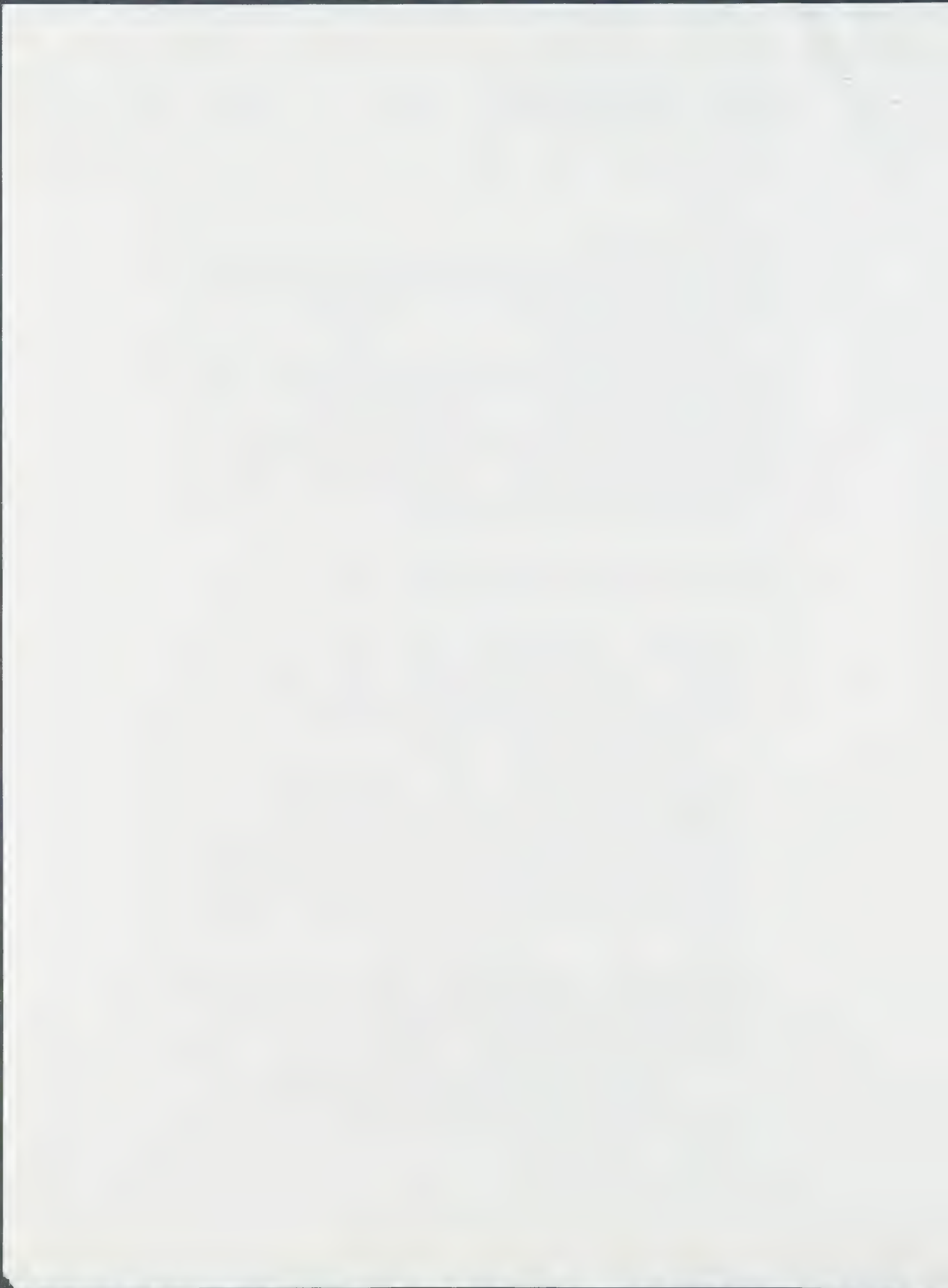
The ANSI standard Z39.1-1986 "Hazardous Information on Chemicals - Prescriptive Labeling" describes the labeling practice of the industry and is applicable to this case. Section 4.1 of this standard states "Hazardous chemical shall be labeled for its immediate and delayed hazards. These hazards are its reasonably foreseeable physical, health, and environmental hazards."

11. The OSHA regulation, 29 CFR 1910.1200, known as the "hazard communication standard" requires that "chemical manufacturers and importers shall evaluate chemicals...to determine if they are hazardous" (section (a)(1)); and further requires that "chemical manufacturers (and) importers...shall describe in writing the procedures they use to determine the hazards of the chemicals they evaluate." (section (b)(2)(ii)).

The hazard communication standard also requires that "the chemical manufacturer, importer or distributor shall insure that each container of hazardous chemicals leaving the workplace is labeled, tagged, or marked with the following information:

- 1) Identity of the hazardous chemicals;
- 2) Appropriate hazard warnings; and





Name and address of the manufacturer, importer, or other responsible party."

With respect to Material Safety Data Sheets, the Hazard Communication Standard requires that "chemical manufacturers and importers shall obtain or develop a material safety data sheet for each chemical substance they produce or import." and that "the material safety data sheet shall be in English and shall contain at least the following information:

- (i) The identity used on the label;
- (ii) The physical hazards of the chemical, including the potential for explosion, and reactivity;
- (iii) The general handling and use instructions which are recommended by the chemical manufacturer or importer for the material safety data sheet.

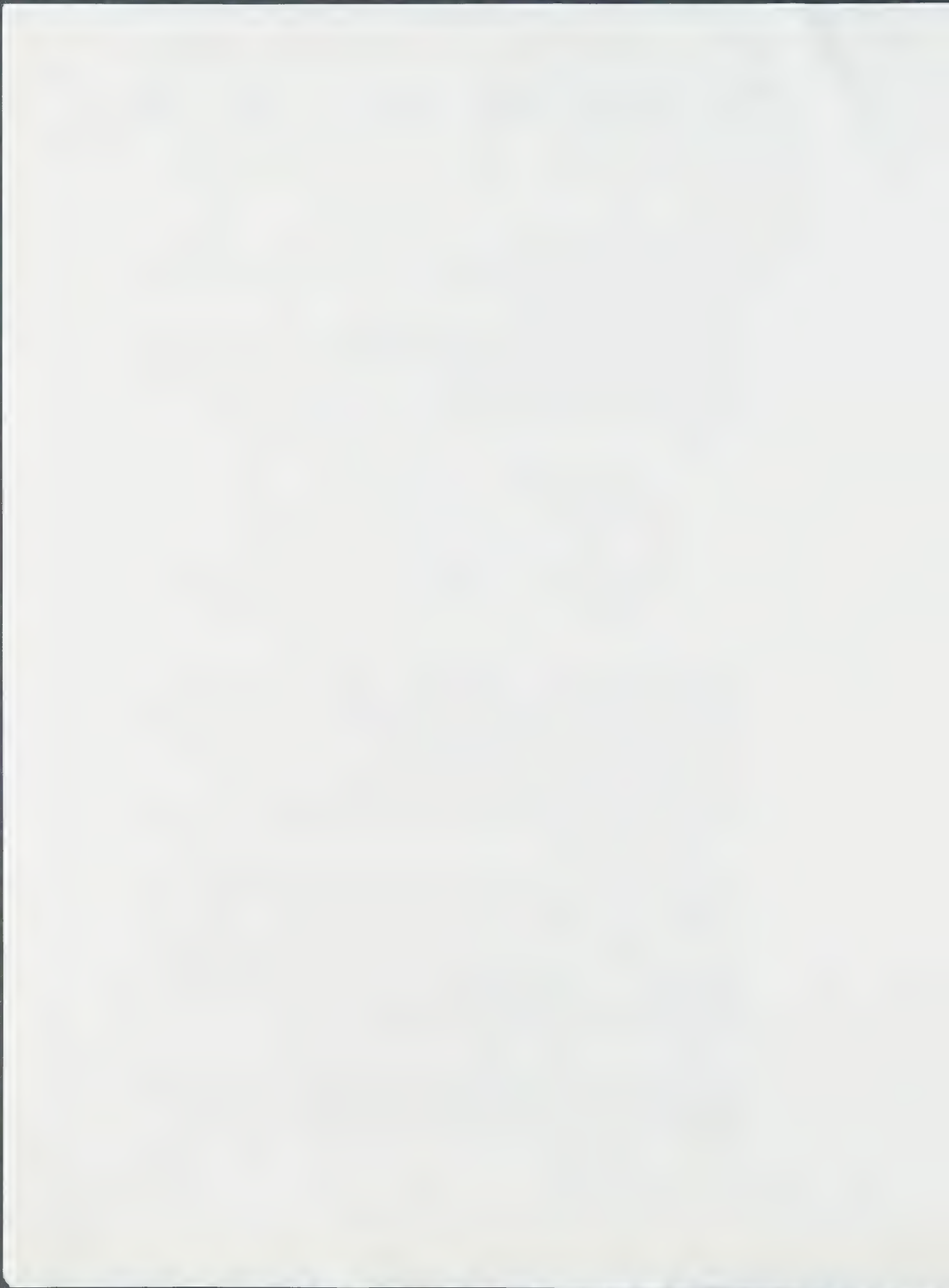
Beginning in 1987 in addition to the above ANSI and OSHA requirements it was the practice of many manufacturers of laboratory chemicals to use graphic pictorial symbols that described the hazard for hazardous chem

Manufacturers of laboratory chemicals have included an example of such graphic pictorial symbols for benzoyl peroxide, an example of which is attached.

- 1. In addition to the above ANSI and OSHA standards, the practice of the industry to warn against the hazardous sensitivities of chemicals, which are known to be sensitive to light, is an example of such graphic pictorial symbols known by American Tokyo Kasei, Inc. as per attached. This was known or should have been known by the industry and plain common sense dictates that users and handlers must be warned.

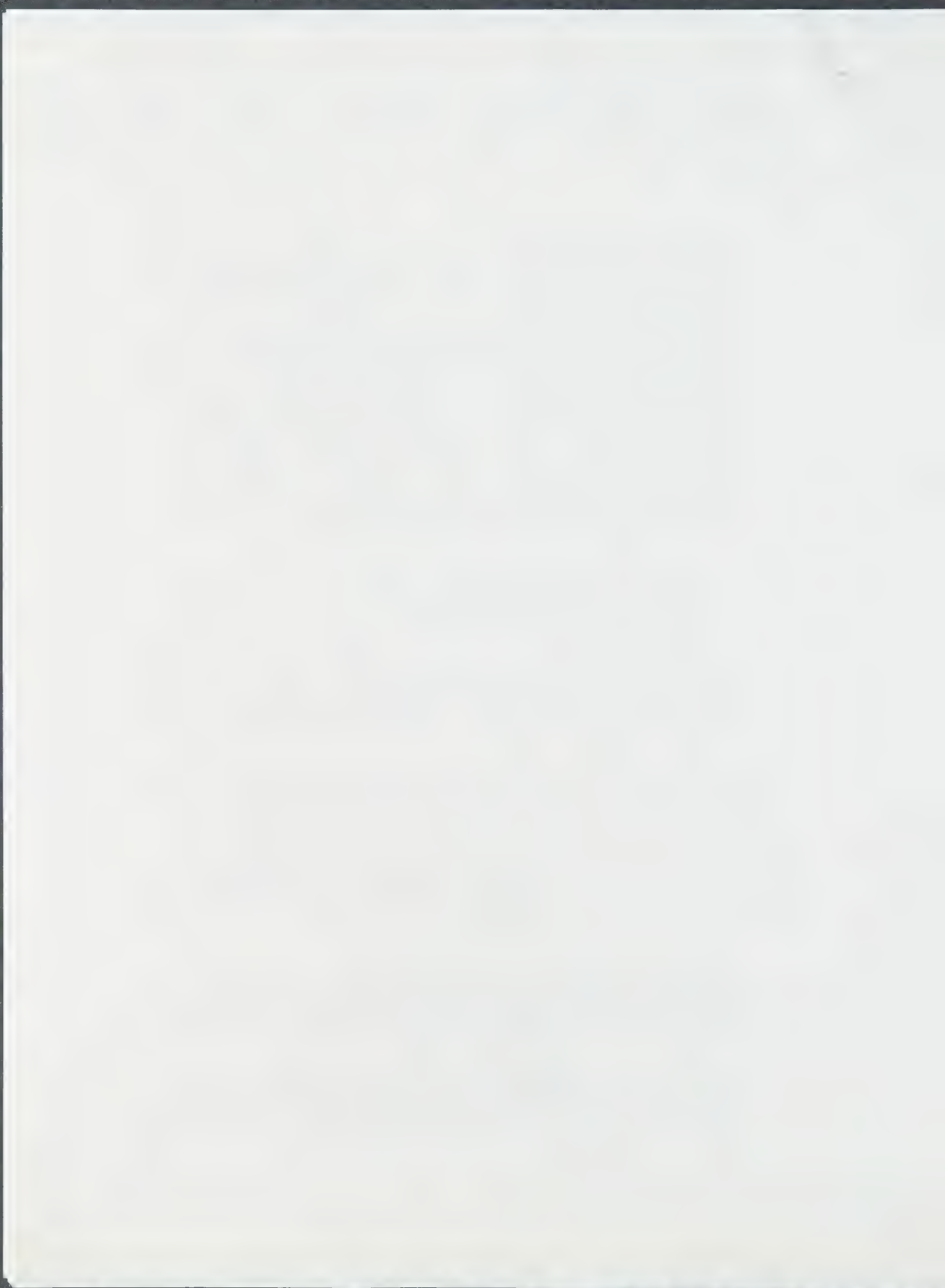
2 /

When I suspected they might be dangerous their distributor was silent on the matter of the hazardous nature of dimethyl azodicarboxylate. The distributor should have at least warned their customers.









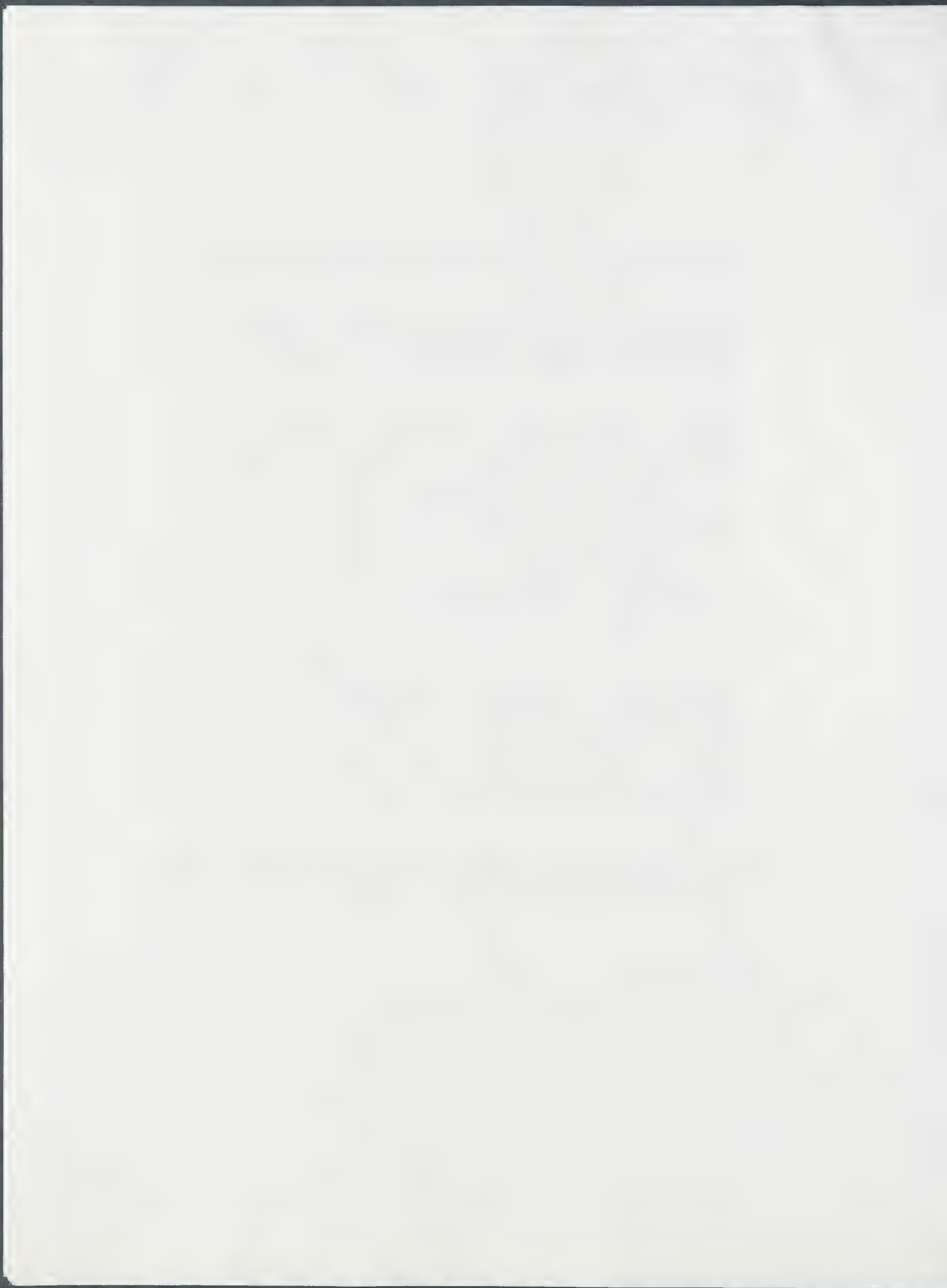
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# AZODICARBOXYLATES: METHYL, ETHYL, t-BUTYL AND BIS(2,2,2-TRICHLOROETHYL)

## WARNING

It has been learned that a sample of methyl azodicarboxylate (*Org. Synth.*, Coll. Vol. IV 1963, 411) violently decomposed during a distillation using an electrically heated mantle as a heat source.

It is again strongly recommended that distillation of methyl azodicarboxylate be carried out from a thermally controlled bath in an electrically heated mantle for the latter may overheat the material being distilled. The bath should have a thermometer in it to keep track of the bath temperature, which should not be allowed to go higher than 130°C. The bath should be covered at the end of the distillation. The distillation should be shielded on all sides by used shielding as described in *Proced. Practices for Handling Hazardous Chemicals in Laboratories* - National Academy Press, Washington, DC (1981), pp. 170-171; see also *Org. Synth.* Coll. Vol. IV 1963, 411.

Tests show that other methyl azodicarboxylates can be decomposed by shock or heat (C. S. Snappard, H. F. Eshack, and G. D. Mager, *J. Polym. Sci. Polym. Chem. Ed.* 1961, 19, 2481). Many azodicarboxylates are thermally unstable and are easily decomposed by shock or heat. The decomposition products of the azodicarboxylates are highly explosive and are always the preferred method.

Snappard, Eshack and Mager have shown that the decomposition of azodicarboxylates in solvent (e.g. methylene chloride or benzene) is the preferred method by which all of the azodicarboxylates to 70% methyl azodicarboxylate, gives products that are easily decomposed by shock or heat. The decomposition products of the azodicarboxylates are highly explosive and are always the preferred method.



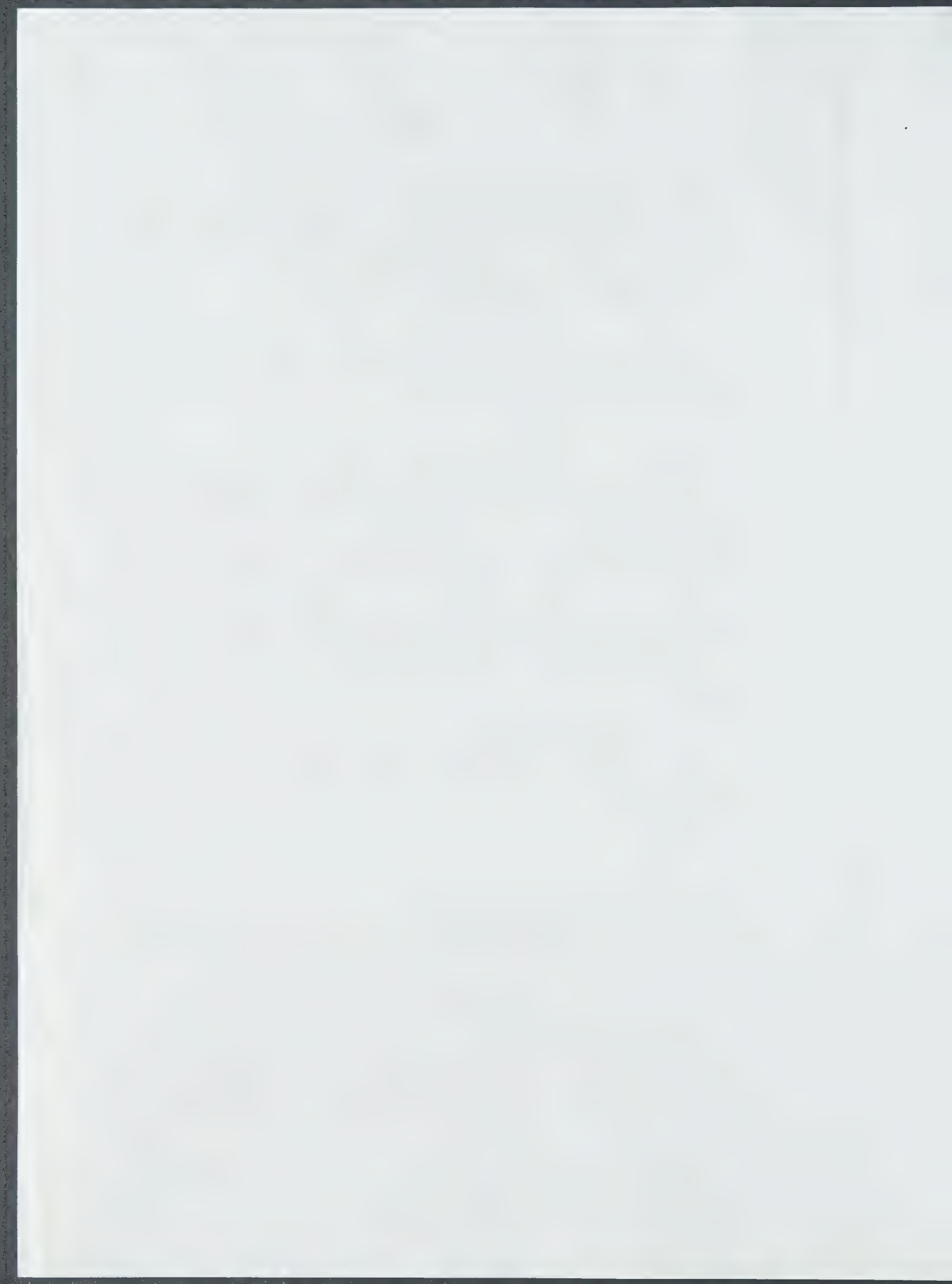


There are no instances of explosions with t-butyl azodicarboxylate (Org. Synth., Coll. vol. VI, 1973, 180) or with 2,2-dimethylazodicarboxylate (Org. Synth., Coll. vol. VI, 1973, 180) which would be expected to be less prone to explosion than the methyl azodicarboxylate because of their higher molecular weights. Nevertheless, for safety they too should be prepared and handled behind good shielding and if they are to be kept for a long time stored in a shock-stable solvent as recommended.

4/2/66









Ziel bis jetzt nicht erreicht werden konnte, so führte doch die Beschäftigung mit den erwähnten Stoffen zur Entdeckung einer Reihe eigenartiger Spaltungs- und Zerfallsreaktionen. Auch zu Beginn der vorliegenden Untersuchung, die sich in der Hauptsache mit einer anderen merkwürdigen Reaktion der Azokörper beschäftigt, wurden einige derartige Zerfallsvorgänge beobachtet, die sich zum Teil als bekanntes anschließen, zum Teil aber auch neu sind und über die sich erst berichten werden soll.

Bei der Behandlung von Azodicarbonamid mit Phosphoroxynitrid in der Hitze tritt ein Zerfall ein in Stickstoff, Wasser, Kohlenoxyd und Blausäure:



und ganz analog beobachtet man die Entstehung von Isocyanaten und Cyantrilen, wenn man die gleiche Reaktion auf substituierte Azokörper anwendet, z. B.



Verwendet man statt der Azoamide ihre sehr leicht zugänglichen Silbererze und läßt Jod auf sie einwirken, so wird gleichfalls Stickstoff frei, und es kommt auch in diesem Falle zur Bildung von Isocyanaten:



Man kann auch Nitrat- und Silbererze

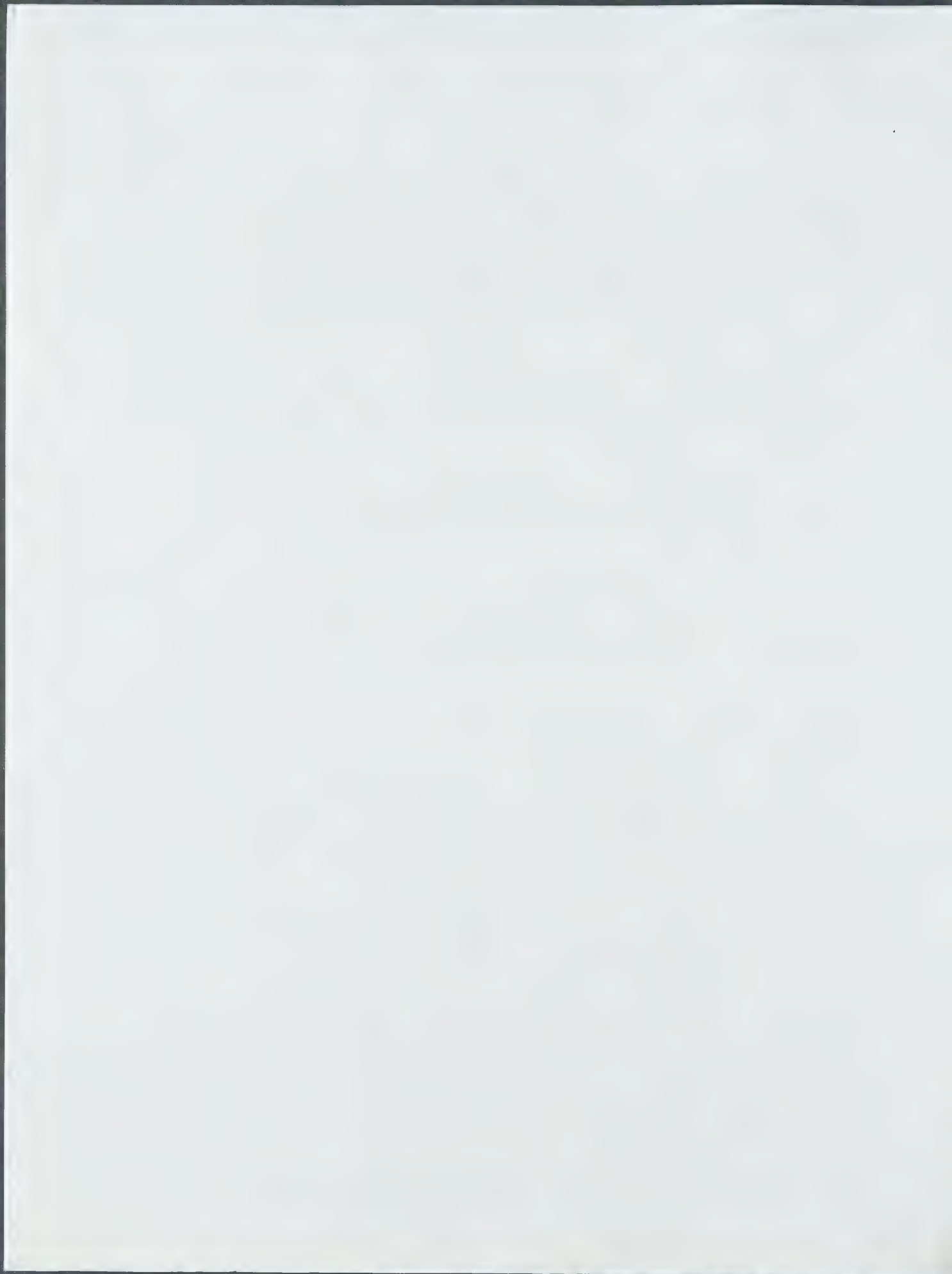


mit konzentrierter Schwefelsäure verändert Azodicarbonamid in eigenartiger Weise. In der Wärme reagieren die beiden Ammonium sehr lebhaft mit einander und außer Schwefeldioxyd, Kohlenoxyd, Kohlendioxyd und Stickstoff erhält man keine nennenswerten Mengen von charakterisierbaren Reaktionsprodukten.

Arbeitet man dagegen bei tiefer Temperatur, so entsteht außer dem eben erwähnten, gasförmigen Verbindungen auch noch Hydrazin, Ammoniak und wenig Stickstoffwasserstoffsäure.

Es ist sehr merkwürdig, daß die Menge der letzteren — ohne Verbindung auch nur einer Spur von Schwefeldioxyd — erheblich zunimmt, wenn man die Zersetzung des Azodicarbonamids mit heißer, konzentrierter Schwefelsäure vornimmt. Als Gase entweichen unter diesen Bedingungen Kohlenoxyd, Kohlendioxyd und Stickstoff, und aus dem Rückstand lassen sich Hydrazin- und Ammoniumsulfat in beträchtlicher Quantität isolieren.

Die Schwierigkeiten bei der Erklärung dieser verschiedenen Spaltprodukte lassen sich vielleicht überbrücken, wenn man eine



### Versetzung des Azodicarbon-diäthylamid-silberj

von Alkyldiaminen

Das Silberjodid wird das Silberjodid in absolutem Äther gelöst und in kleinen Portionen unter zeitweiligem Schütteln die berechnete Menge Jod in absolutem Äther hinzugefügt. Es scheidet sich Jodsilber aus, die Lösung nimmt den heftigen Geruch nach Isocyanat an, und der frei werdende Stickstoff läßt sich an dem im Innern der Flasche sich bildenden Druck erkennen.

Das ätherische Filtrat wird durch Silberschwamm von den letzten Spuren Jod befreit und mit Phenylhydrazin versetzt.

Es fällt alsdann nach Bildung einer gallertartigen Trübung beim Erhitzen in Eis eine reichliche Menge von Äthyl-phenyl-semicarbazid ab, das nach dem Schmelzen aus, das nach der Umkrystallisation aus absolutem Alkohol einen Schmelzpunkt von  $135^{\circ}$  besitzt.

0,1000 g Subst. (in. Vak. über  $H_2SO_4$  getrt.): 0,4084 g  $CO_2$ , 0,1199 g  $H_2O$ , 0,0110 g  $N_2$  (aus 0,0100 g  $CO_2$ , 0,1123 g  $H_2O$ , — 0,1579 g Sbst.: 81,7 ccm  $N$  (19°, 768 mm) — 0,1450 g Sbst.: 29,2 ccm  $N$  (19°, 768 mm).

Calc. für  $C_{10}H_{12}N_2$ : Ber. C 60,35, H 7,26, N 23,46.

Geft. = 60,22, 60,40, = 7,84, 7,33, = 23,39, 23,25.

### Herstellung von Hydrazo-dicarbonensäure-dimethylester

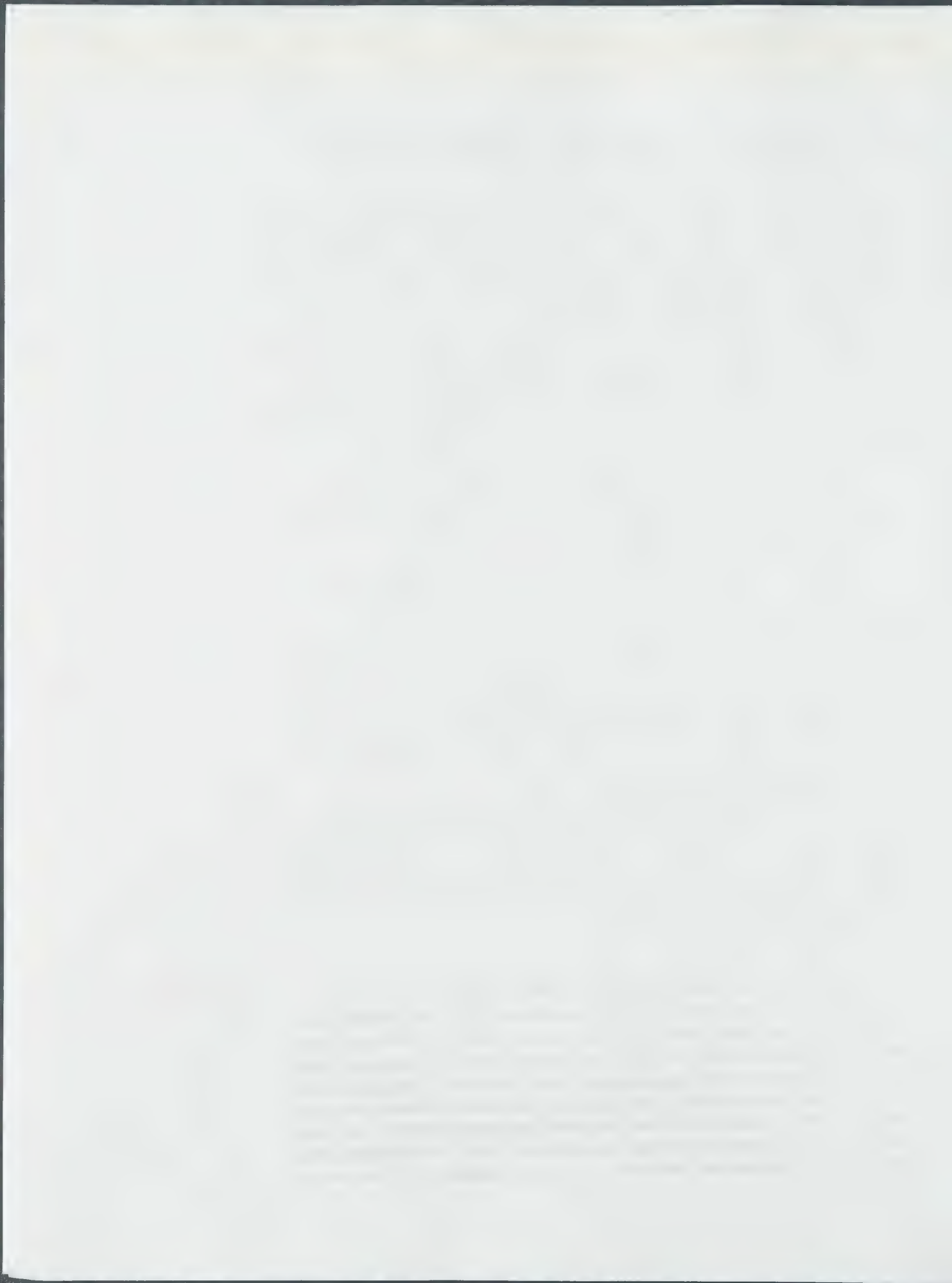
Das Parazinhydrat werden mit 50 ccm Alkohol vermischt und diese Mischung zu 200 ccm Äther gegeben, so daß eine trübe Suspension entsteht. In Flüssigkeit wird am Rückflußkühler zum Sieden erhitzt, während man unter beständigem Schütteln ein Gemisch von 19,6 g Chloroform und 19,6 g Dimethylester mit 30 ccm Äther tropfenweise hinzugefügt. Nach dem Abtragen ist, wird noch 15 Minuten erhitzt, das Gemisch abfiltriert und das ausgeschiedene Hydrazinchlorhydrat abfiltriert.

Das Filtrat scheidet sich beim langsamen Eindampfen der Flüssigkeit in schönen, zu sterbförmigen Büscheln vereinigten, Kristallen ab. Durch Umkrystallisieren aus alkoholhaltigem Äther erhält man die Verbindung rein und in einer Ausbeute von 10 g (100% der Theorie) erhalten.

Schmelzpunkt bei  $132^{\circ}$ .

### Herstellung von Azodicarbonensäure-dimethylester.

Das Dimethyldiazodicarbonensäure-dimethylester werden in 20 ccm konzentrierter Salpetersäure (1,4) gelöst und zu dieser Lösung 50 ccm Chloroform hinzugefügt. Unter guter Eiskühlung läßt man alsdann unter Schütteln zu diesem Gemisch eine rauchende Salpetersäure schnell zutropfen und das Gemisch 10 Minuten unter öfterem Umschütteln in Eis stehen. Hierauf wird die Chloroformlösung von dem hellgelben Salpetersäuregemisch getrennt, dreimal mit Wasser gewaschen, die Lösung filtriert, mit 20 ccm Äther verdünnt, das Chlorcalcium getrocknet, auf dem Wasserbad die Hauptmenge





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Chemicals*



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113 5755 250  
Chem #11946  
AVAILABLE IN BULK

**Diethylcarbamoyl Acid Ammonium Salt**

111 2184 1000  
Chem #11947  
AVAILABLE IN BULK

118 0421 1000  
Chem #08703  
AVAILABLE IN BULK  
TSCA  
HNZ 29, 1000  
EHSF 2001

112 8800 1000  
Chem #01421  
AVAILABLE IN BULK

**Acid Lecter**

12 8814 1000  
Chem #01121  
AVAILABLE IN BULK

**Acetone**

119 5711 1000  
Chem #11948  
AVAILABLE IN BULK

**Azidosulfonylbenzoic Acid see p-Carboxybenzenesulfonyl**

**Zincdiethanol see N-(2-Hydroxyethyl)ethyleneimine**

108 2924 1000  
Chem #10333-3  
MW 182.26  
C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>  
mp 68°C (lit)  
Appearance: Orange crystals  
Assay By UV-VIS  
Hydroxybenzene content (by IR) 1.0% (max)  
Africa Index 11 930



**Azobisisobutyronitrile**

170 2471 5000  
Chem #07249  
TSCA  
KSP 500



**4-Cyanopentanoic Acid**

104 4171 5000  
Chem #07210  
REFERENCE GRADE  
TSCA

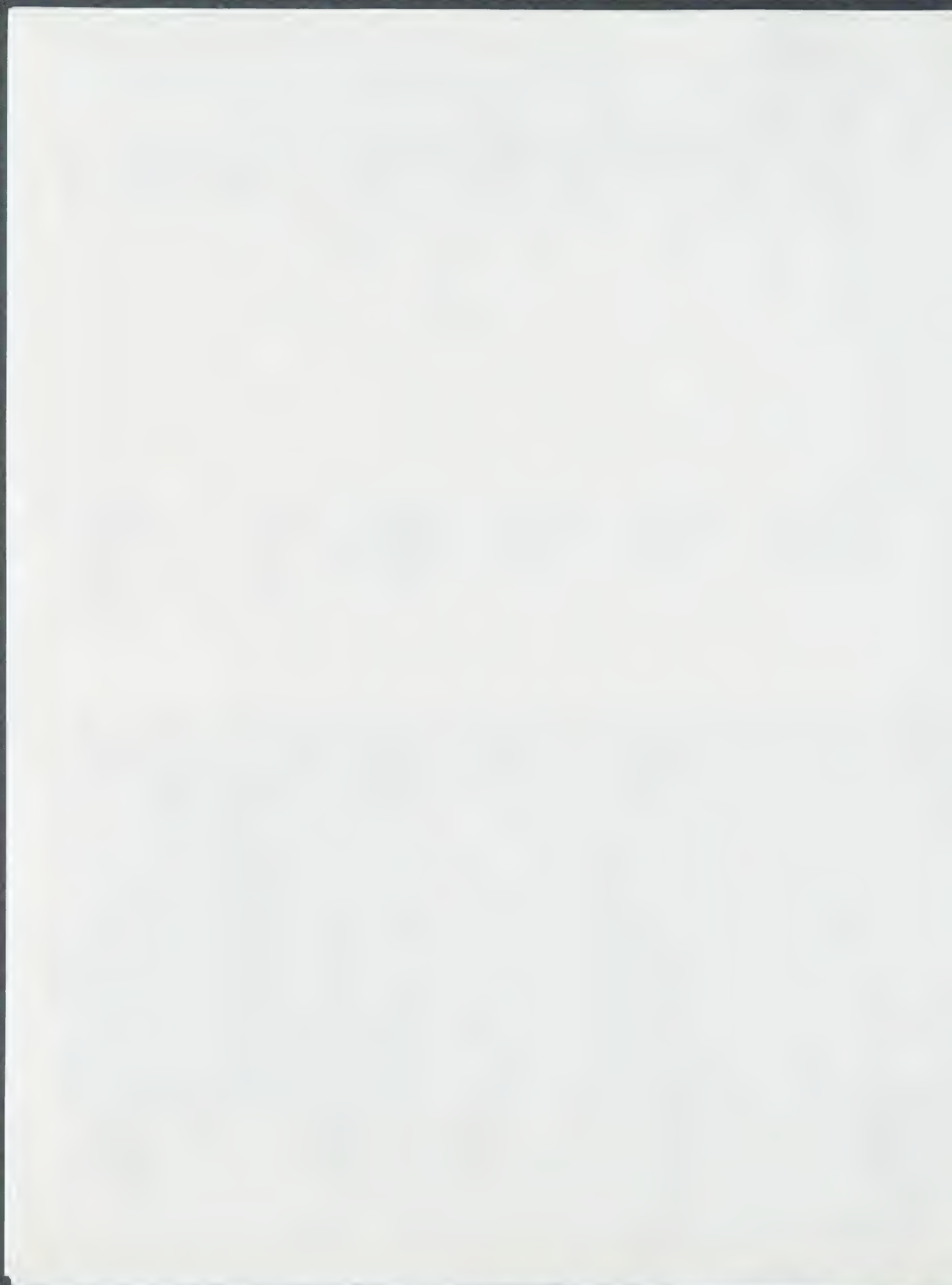


118 4746 1000  
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## Disposal

Each chemical listing in this catalog contains information on the proper methods for the disposal of the chemical. This information is identified by a three digit number followed by the disposal method. This information is identified by a three digit number which is defined below:

- 100 Flush to sewer with copious amounts of water
- 101 Neutralize with sodium bisulfate and flush to sewer with copious amounts of water
- 102 Neutralize with sodium bicarbonate and flush to sewer with copious amounts of water
- 103 Dispose of in an approved chemical incinerator. Compounds containing halogens or sulfur and suspected carcinogens should be disposed of in an incinerator equipped with an after burner.
- 104 Dispose of in an approved chemical landfill.
- 500 Uncontaminated material may be disposed of in a sanitary landfill. Check local codes.

Solids being incinerated should be appropriately packaged as necessary for safe feed to the incinerator or dissolved in compatible waste solvents prior to incineration. Follow all label warnings when handling or disposing of waste chemicals. Discharge, treatment, or disposal may be subject to Federal, state and local laws. These disposal guidelines are intended for the disposal of catalog-size quantities only.

We must emphasize that the ultimate effect on the disposal of chemicals are frequently changing at Federal, state, and local levels of government. If at-site treatment or disposal facilities are not available or you are not thoroughly familiar with all applicable disposal regulations in your locale, then we suggest that you contact with a licensed waste disposal service. It is the customer's responsibility to determine the appropriateness of any disposal method. For assistance in determining the appropriate waste disposal contractor in your area call 1-800-225-6572.

## Labels and Material Safety Data Sheets (MSDS)

The labels of KODAK Chemicals provide the information necessary for safe handling of our products. The information is presented in a limited space and will allow the user to determine the appropriate safety precautions to be taken. The information is presented in a format that is more than the molecular weight and molecular formula.

When there are changes in chemical names, the label should be encircled in normal type. The label should be replaced with the new label in accordance with the instructions that are provided for the present-day labeling of chemicals. The label should be replaced with the new label in accordance with the instructions that are provided for the present-day labeling of chemicals.

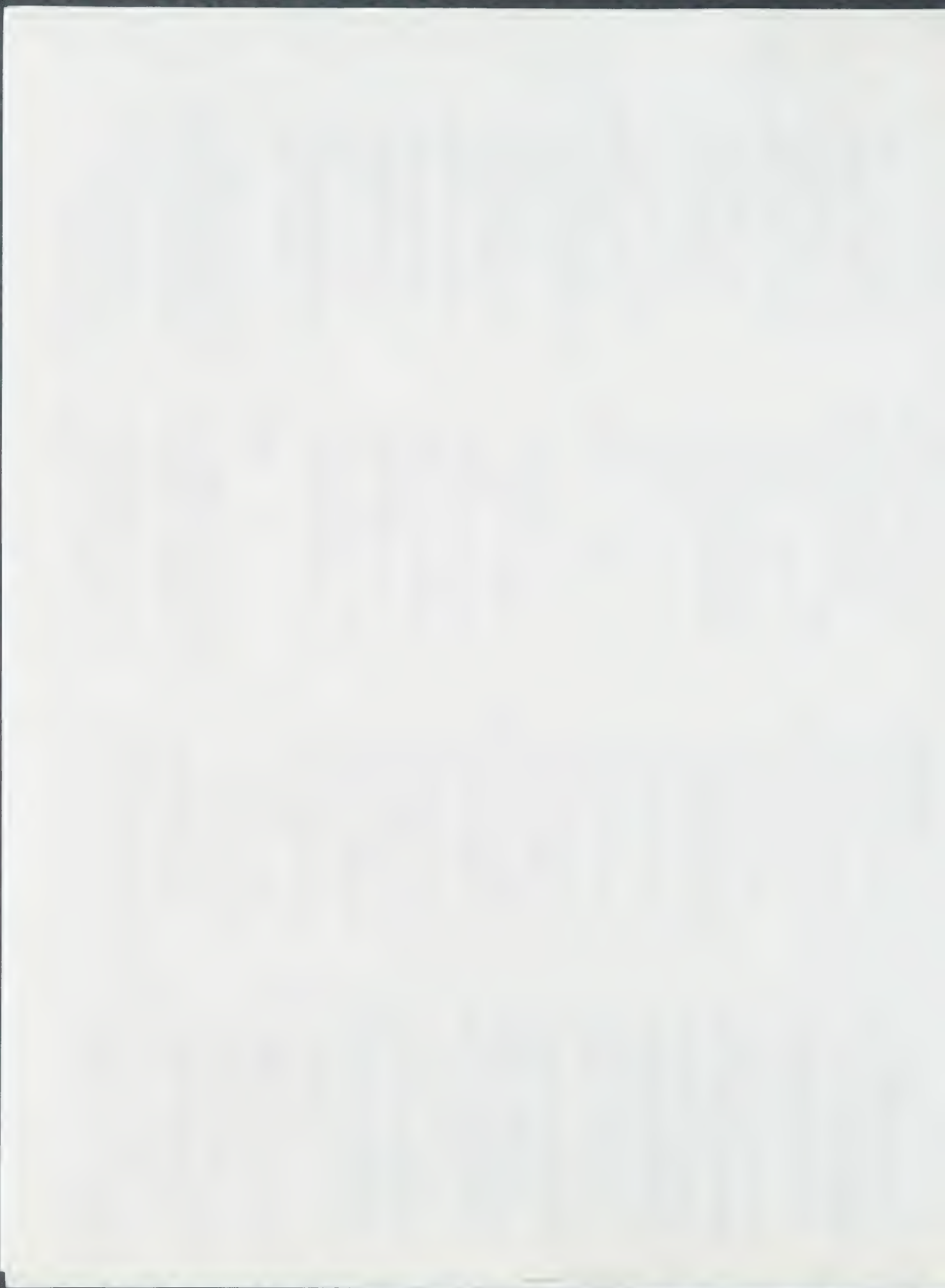
For more information on the safety information at the time of purchase, please refer to the Material Safety Data Sheet (MSDS) entry in this catalog. The information is presented in a format that is more than the molecular weight and molecular formula. The information is presented in a format that is more than the molecular weight and molecular formula.

- 101 MAY CAUSE ITCHING IRRITATION BASED ON ANIMAL DATA
- 102 MAY CAUSE CARDIAC DAMAGE BASED ON ANIMAL DATA
- 103 IRRITATION (USES EYE IRRITATION)
- 104 HARMFUL IF INHALED
- 105 IRRITATION (USES EYE IRRITATION)
- 106 IRRITATION (USES EYE IRRITATION)
- 107 HARMFUL IF INHALED OR ABSORBED THROUGH SKIN
- 108 HARMFUL IF INHALED OR ABSORBED THROUGH SKIN
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- 123 HARMFUL IF INHALED OR ABSORBED THROUGH SKIN
- 124 HIGH VAPOR CONCENTRATIONS MAY CAUSE DROWNING
- 125 GAS REDUCES OXYGEN AVAILABILITY FOR BREATHING
- 126 VAPOR REDUCES OXYGEN AVAILABILITY FOR BREATHING
- 127 POTENTIAL PEROXIDE FORMER
- 128 THE TOXICOLOGICAL PROPERTIES OF THIS MATERIAL HAVE NOT BEEN DETERMINED
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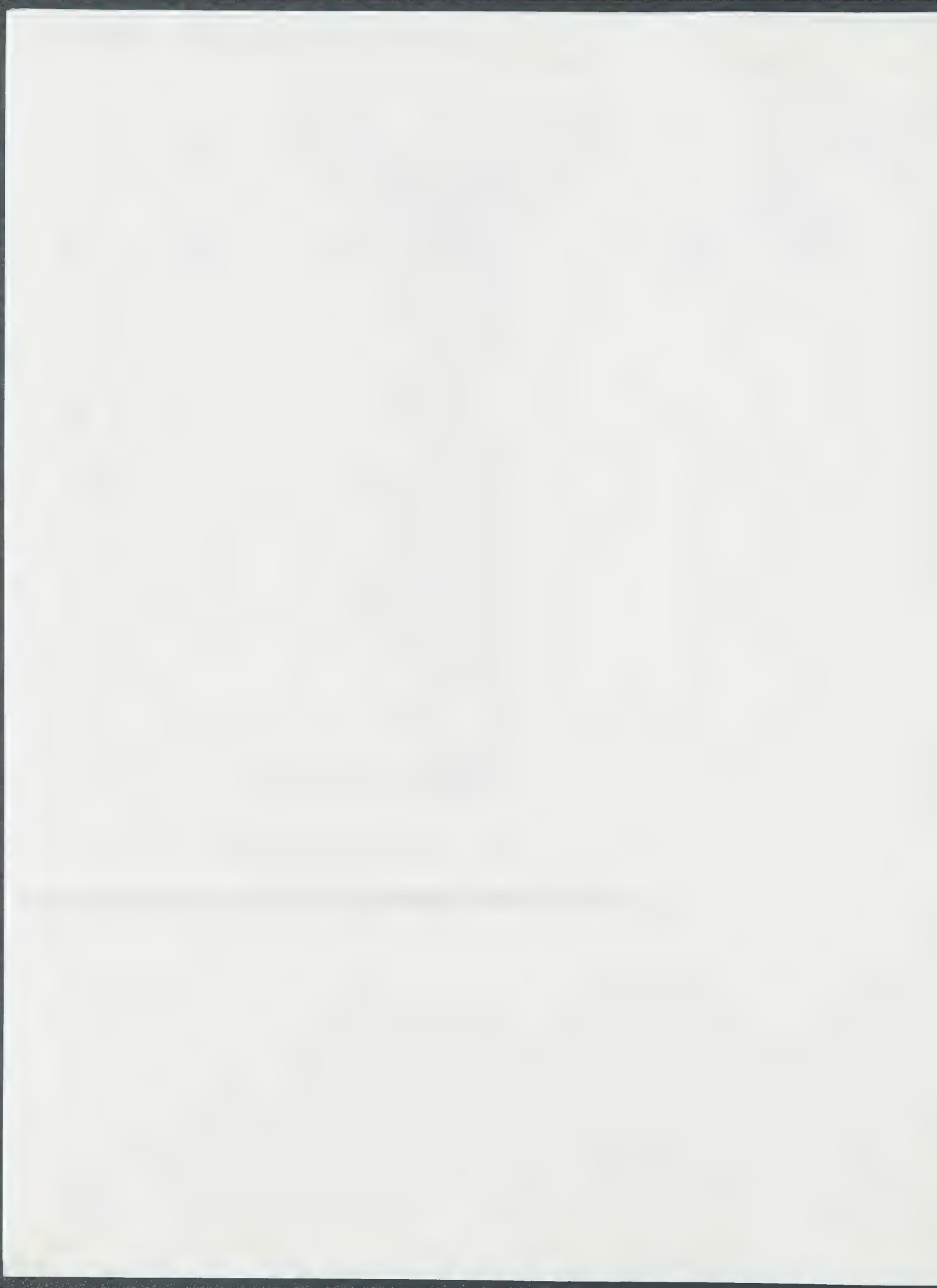












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FAX FROM : 4142770709

ALFRED BADER FINE ARTS

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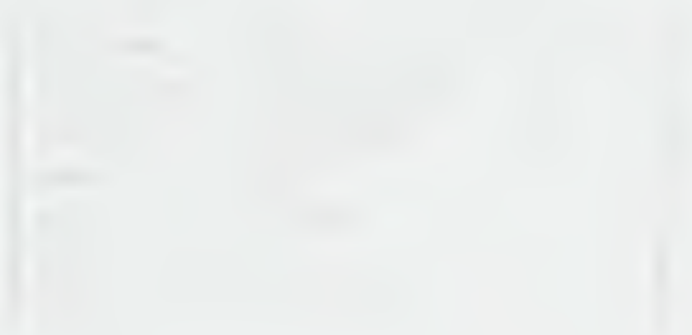
MEMORANDUM FOR THE RECORD

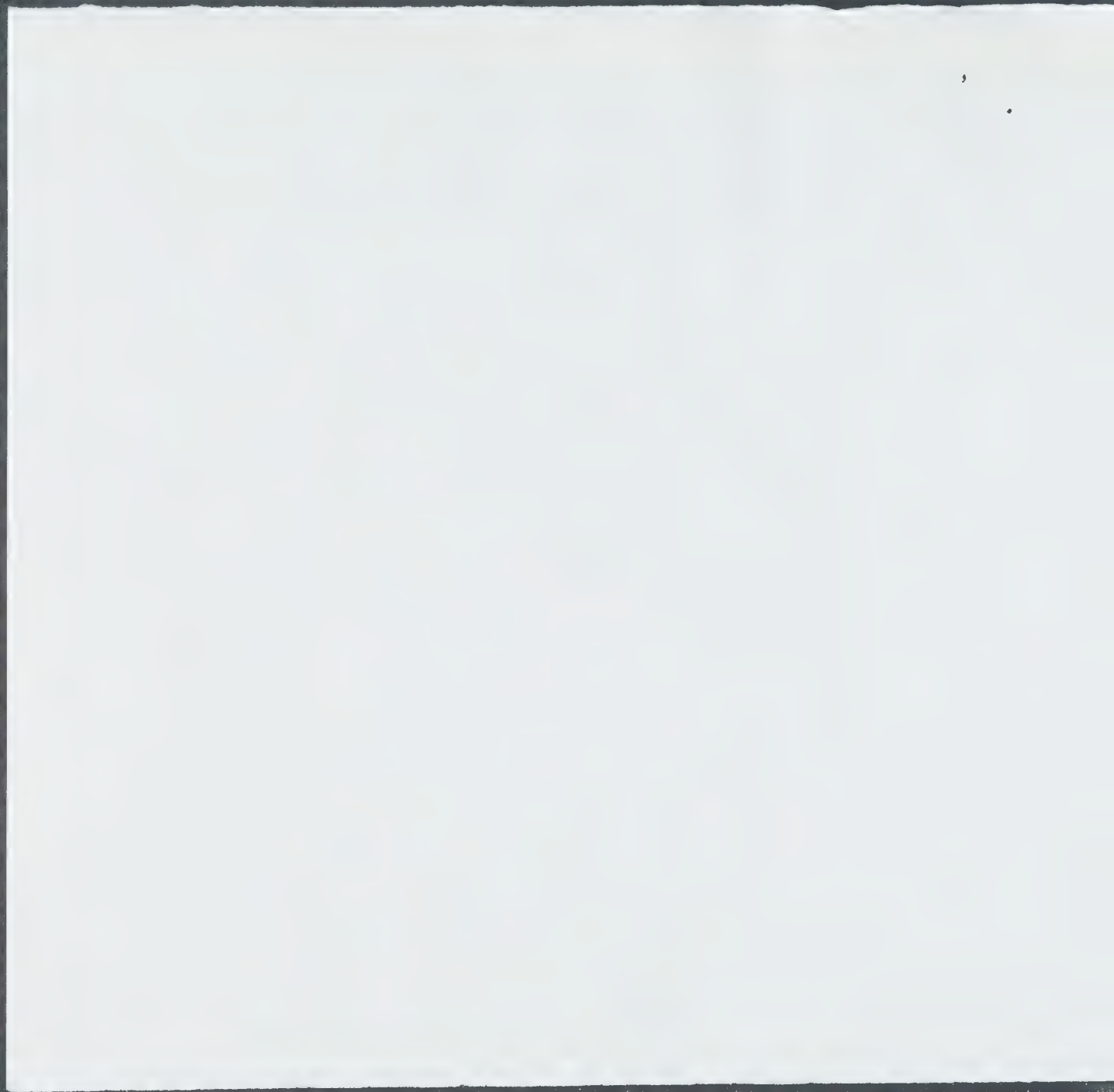
1952



STATEMENT OF WORK

1.0 PROJECT OBJECTIVES





FAX FROM



DR. ALFRED R. BADER  
52 Wickham Avenue  
Bexhill-on-Sea  
East Sussex TN39 3ER  
Telephone/Fax: 0424-22-22-23

Date: July 9 1995

Page 1 of 1

To: Dr. Maria Isano  
Fax: President, T.C.I. America

Dear Dr. Isano:

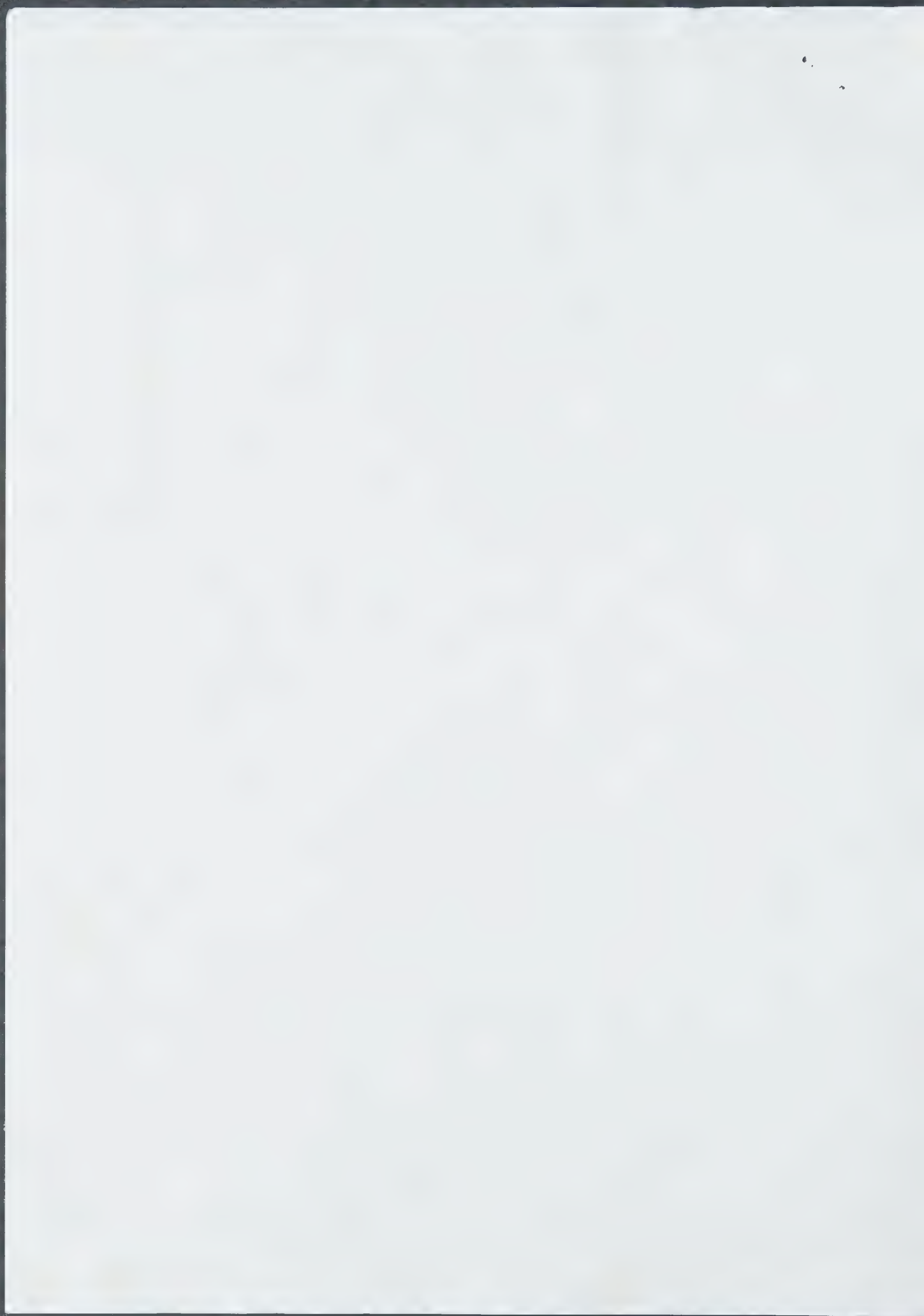
Thank you for your fax of July 5.  
I will be happy to talk to your lawyer  
after my return to Milwaukee on July 28.

Aldrich has had many lawsuits  
similar to the one you describe: I call  
them "blackmail lawsuits". I worried  
about the first few & then got used to them.  
They are usually settled before coming to court -  
much depends on the ability of your lawyer.

Please tell Mr. Asakawa that he can  
depend on my help.

Best regards

Alfred Bader





**EXHIBIT**

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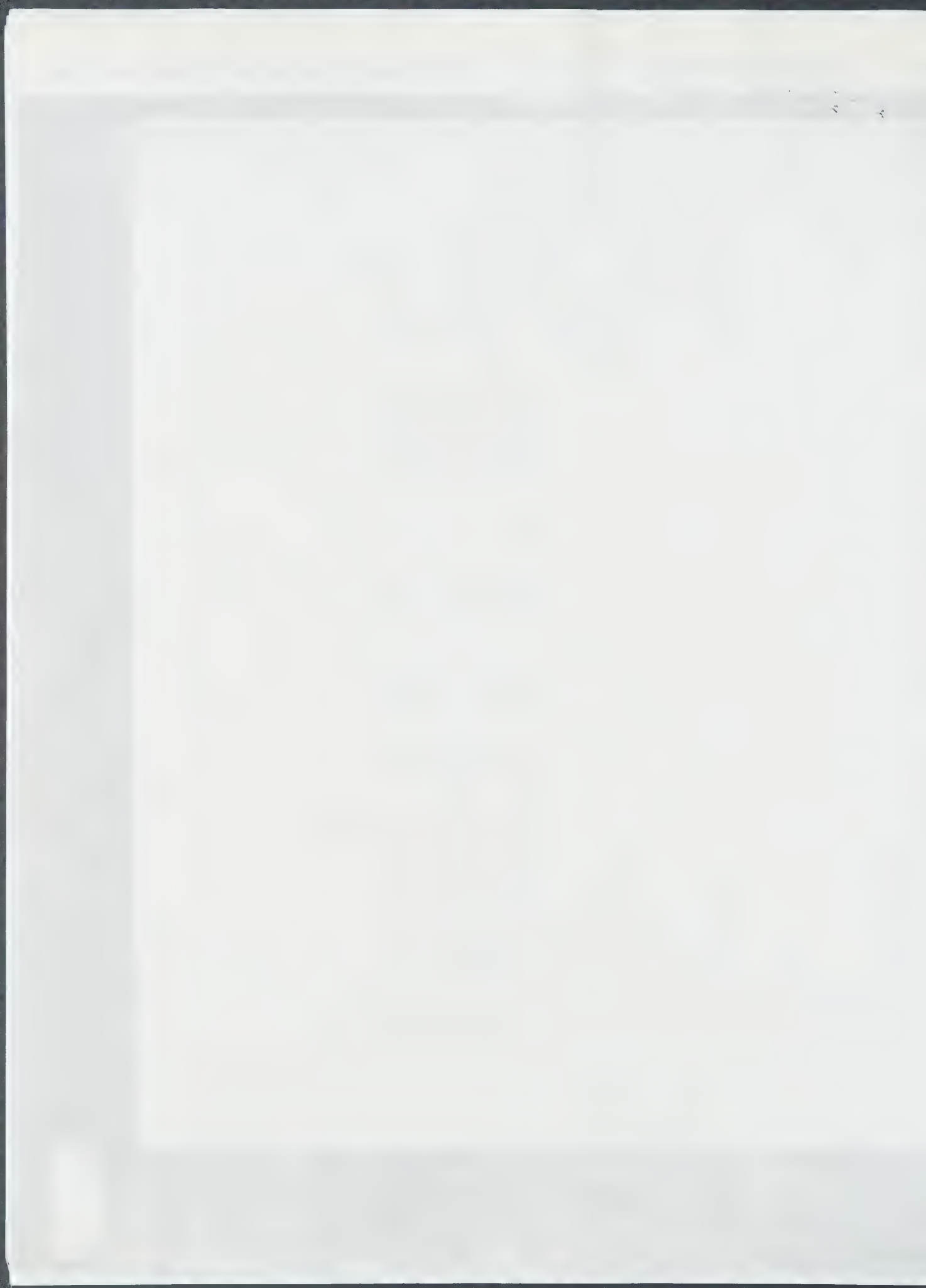
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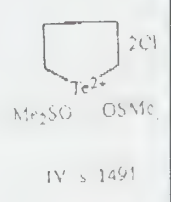


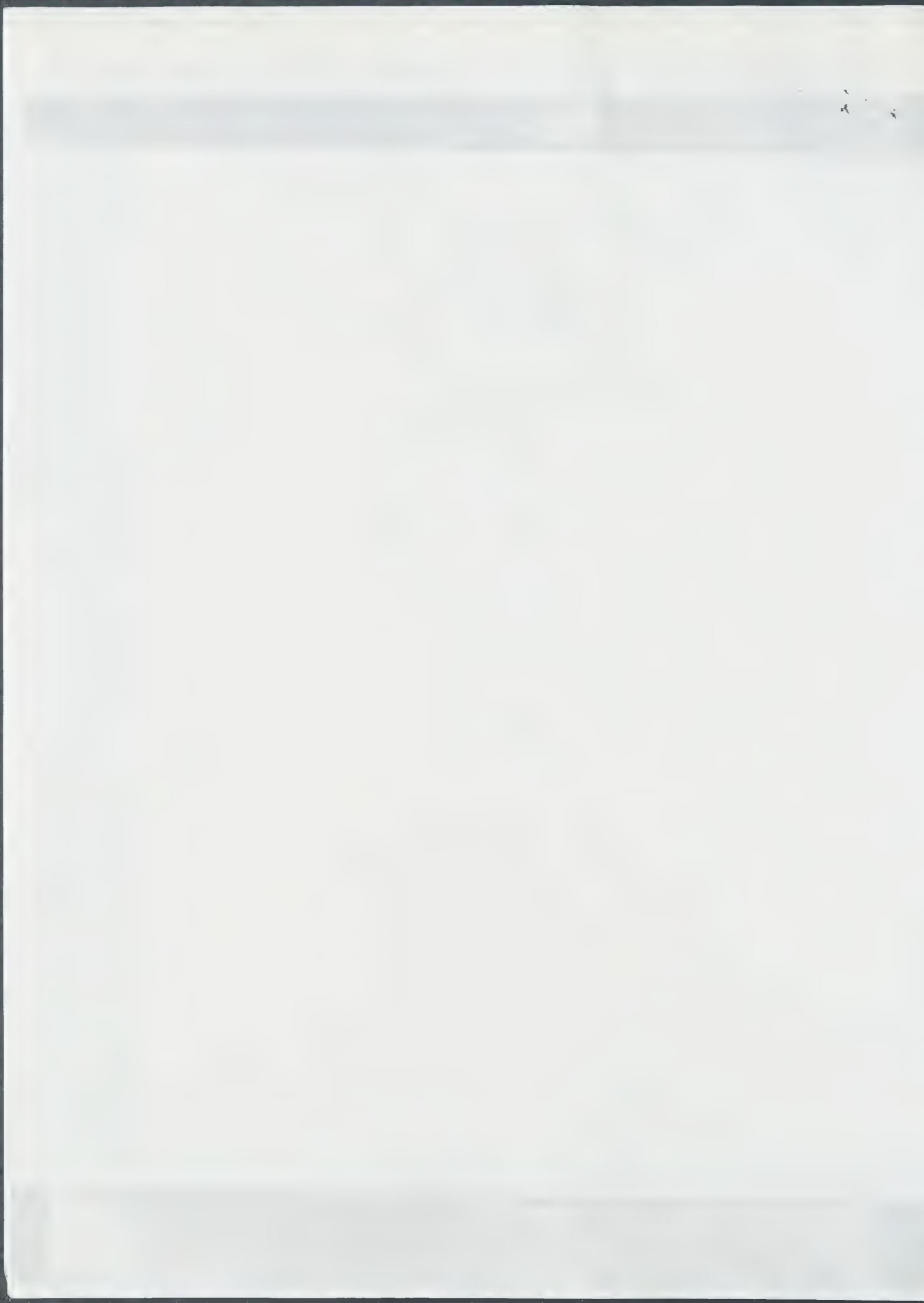






CONTENTS











Bretherick's  
Handbook of  
**Reactive  
Chemical  
Hazards**

Fourth Edition

J. BRETHERICK, Ph.D., Editor in Chief

Volume 1: Organic Compounds  
Volume 2: Inorganic Compounds  
Volume 3: Polymers

1911  
1912  
1913  
1914  
1915

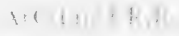
- Phenylvanadium(V) dichloride oxide, 2111
- Tetraphenyllead, 3571
- 2-, 3- or 4-Tolylcopper, 2573
- Triphenyltin bromide, 3455
- Triphenyltin bromide ethoxy, 3455
- Triphenyllead nitrate, 3487

ARYL HYDRAZINE ACETATE PERCHLORATES



Ar = H, Me, Et, n-Bu, i-Bu, t-Bu, Ph, etc

ARYL 1-VINYLETHER DERIVATIVES



In the preparation and use of a series of previously substituted aryl 1-vinylether derivatives (Ar = phenyl, p-tolyl, m-tolyl, o-tolyl, n-butyl, isobutyl, t-butyl, cyclohexyl, etc.) the following results were obtained:

ASSESSMENT OF RELATIVE CHEMICAL HAZARD

1. Comparison of the relative hazard of the above series of compounds was made using the following criteria:
  - (a) Boiling point (BP) (°C)
  - (b) Melting point (MP) (°C)
  - (c) Density (D) (g/cm<sup>3</sup>)
  - (d) Vapor pressure (VP) (mm Hg)
  - (e) Flash point (FP) (°C)
  - (f) Autoignition temperature (AIT) (°C)
  - (g) Decomposition temperature (DT) (°C)
  - (h) Solubility in water (S) (g/100 ml)
  - (i) Toxicity (LD<sub>50</sub>) (mg/kg)
  - (j) Corrosivity (C) (pH)
  - (k) Reactivity (R) (1-5)
2. The relative hazard of the above series of compounds was assessed using the following criteria:
3. The relative hazard of the above series of compounds was assessed using the following criteria:
4. The relative hazard of the above series of compounds was assessed using the following criteria:
5. The relative hazard of the above series of compounds was assessed using the following criteria:
6. The relative hazard of the above series of compounds was assessed using the following criteria:
7. The relative hazard of the above series of compounds was assessed using the following criteria:

Literature source assessment of re relation to the t various situation: the nucleus of a s [1]. Relatively s elevated pressur decomposition a temperatures, qe by these method processes or pre small batch man using simple eq practical aspects

A simple eva substances, inc sensitivity, mech Dow reactive ch in pilot plant c predicting the measurements c scaled cell DS ASTM E-537. derived from t known explosiv thermal decom for measuring assess thermal method in [7] a different DSC specific practi detonation/de derline) chem results compa Added alumin ammonium itrotoluene (7 propagate de would propag the Reactive heating and contained in thermocoupl jacket within pressure whic control unit,





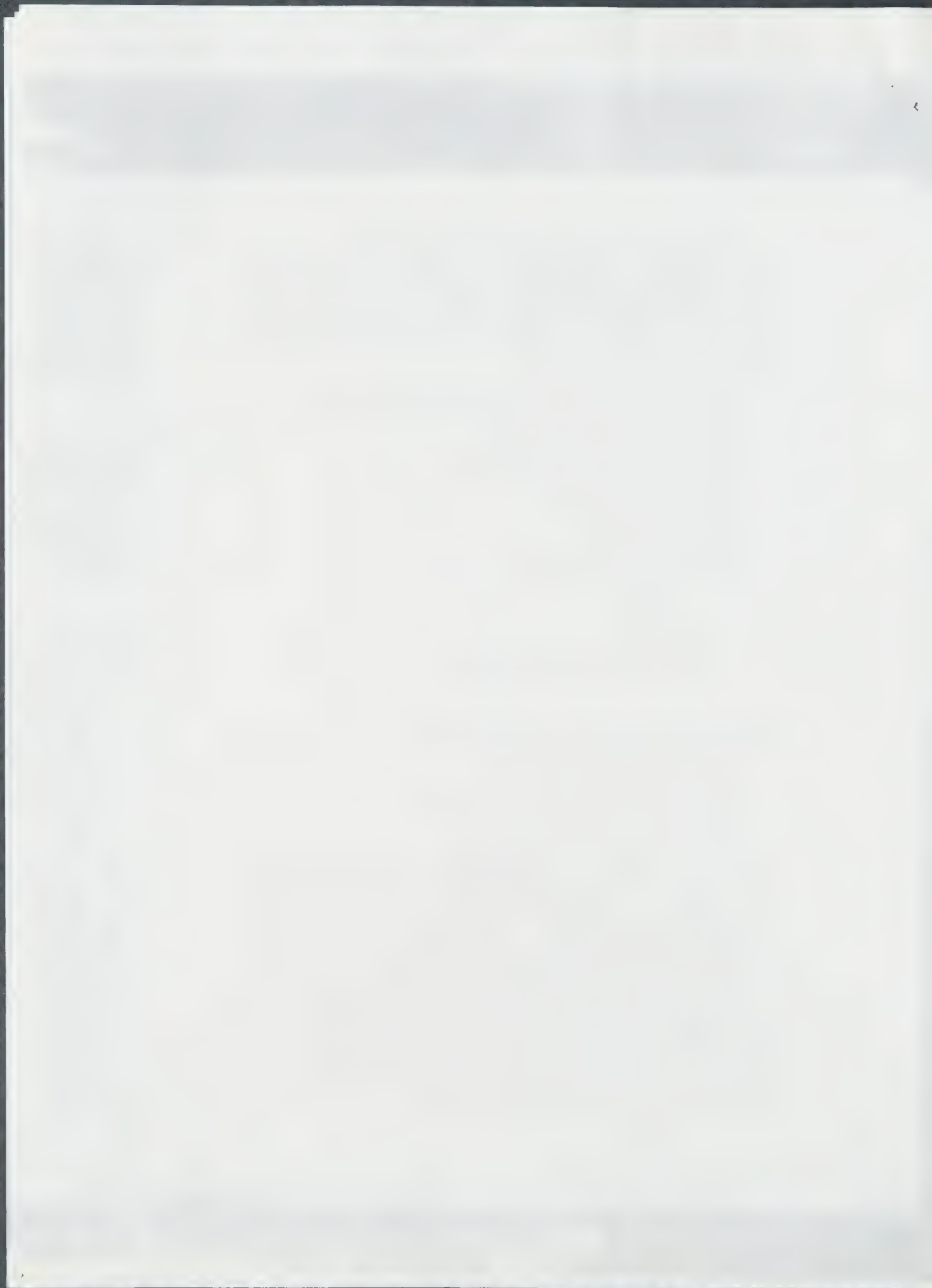














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- 2. Lithium tetrafluoroborate, 4000
- 3. Lithium tetrafluoroborate, 4000
- 4. Magnesium perchlorate, 4000
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- 19. Magnesium perchlorate, 4000
- 20. Magnesium perchlorate, 4000

**COMPRESSION GRADES**

and the whole field of this work is concerned with the conversion of energy into chemical energy and the compression of gases and liquids.

**COMPUTATION OF REACTIVE CHEMICAL HAZARDS**

1. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 12-13
2. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 14-15
3. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 16-17
4. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 18-19
5. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 20-21
6. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 22-23
7. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 24-25
8. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 26-27
9. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 28-29
10. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 30-31
11. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 32-33
12. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 34-35
13. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 36-37
14. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 38-39
15. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 40-41
16. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 42-43
17. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 44-45
18. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 46-47
19. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 48-49
20. H. W. Turner, *J. Appl. Chem.*, 1951, 5, 50-51

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These methods instability in a r between the pa conventional st techniques to st parameters wer was below 10% the 3 stability cr tion, and non-minimising haz

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to compare the results of several computer methods for calculating the heat of formation and mutual reactivity of other compounds. The methods developed and tested. These have been variously based on statistical and empirical thermodynamic parameters, simplified in some cases with experimental data, to produce fast and easy systems.

These methods were jointly evaluated for their ability to predict sensibly and accurately the range of compound types. It was concluded that the reaction parameters considered and chemical stability were far above the range of a statistical analysis. However, application of path reaction parameters was only partially successful. To all angles and over a wide range of conditions, the methods appear to have great potential for the study of explosive behaviour decomposition products, storage, transfer and transportation of chemicals.

A preliminary assessment of the effectiveness of these computer programs was made. It was concluded that explosive power was accomplished in relative to the important aspect of sensitivity to initiation and many other factors were indicated as hazardous. There was a need for a more comprehensive study of the sensitivity of explosives to initiation. The estimate that sensitivity is the most important factor in the handling and transport of explosives should be based on the basis of known sensitivity of initiation. Present data are being provided, etc.

The computer program is a relatively simple program which is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P.

It is intended that the program will be used to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P. The program is designed to calculate the heat of formation of compounds containing C, H, N, O, S, Cl, Br, F, I, and P.















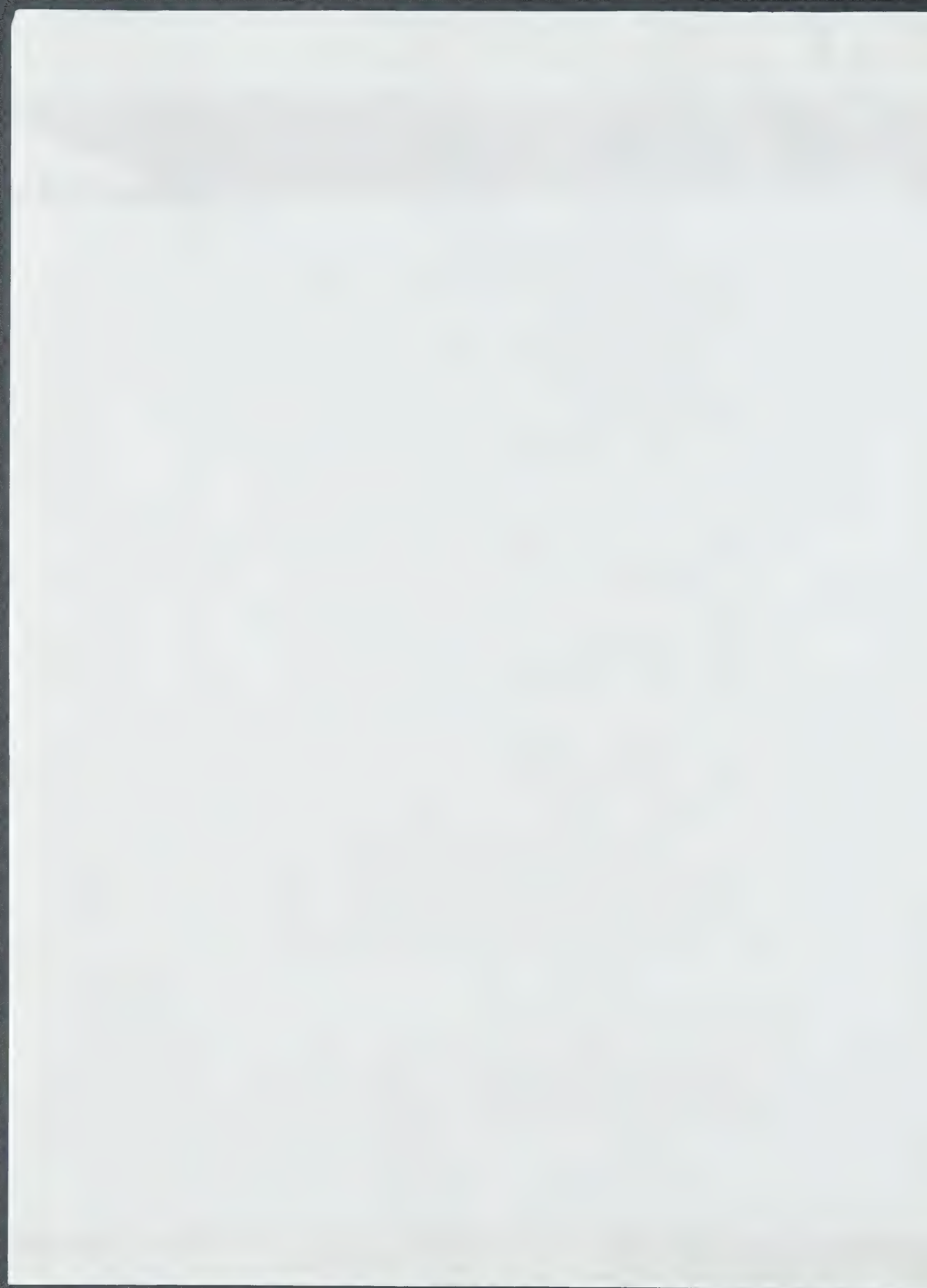














To: Dr. Alfred Bader

Aug 8, 1995

Alfred,

The normal bottle that Aldrich uses will withstand 60-90 psi before bursting.

This lead me to my file on chemical weapons. An article in C&E News May 1, 1995 on the bombing in Oklahoma City states that: "People are killed and frame structures are damaged if hit directly by an overpressure of at least 25 psi."

This is a very low figure in terms of numerical magnitude as we all probably perceive that an explosion would have involved much higher numerical values.

Please don't hesitate to call in the future

Best regards,  
Bob Cengiz



To: Dr. Alfred Barber  
Date: 1/15/52

Alfred,

The normal boiler that Alfred uses will withstand 20-30 psi before bursting.

This led me to my file on chemical weapons, the article in Life News and I have on the bombing in the Bronx. City states that "people are killed and steam structures are damaged if hit directly by an overpressure of at least 25 psi."

This is a very low figure in terms of numerical magnitude as we all probably perceive that an explosion would have involved much higher numerical values.

Please don't hesitate to call in the future.

Best regards,  
Barber



percondensed technology, patented by Exxon in February, the tolerable entrained liquid can be as high as 50 mole %.

Exxon expects to further develop metallocene chemistry with more innovative single-site catalysts. Ziegler-Natta catalysts have catalytic sites of varying activity levels, notes Gregory L. McPhee, vice president of Exxon's Exxpol venture. This produces variations in polymer products, such as variable branching or restricted molecular weight ranges. Single-site catalysts produce more uniform products—allowing incorporation of comonomers and termonomers with more precise compositions and more specific properties.

Joseph Higgins

## Oklahoma bomb shows common items' power

The devastation in Oklahoma City belies the ordinariness of the likely bomb components that caused it.

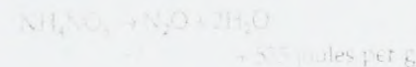
There are many indications a key component was ammonium nitrate, widely used as a fertilizer. Bomb dis-

posal experts say terrorists the world over favor ammonium nitrate, and for good reason: It is cheap, easy to acquire, and effective.

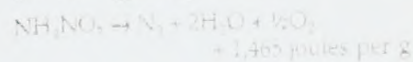
Ammonium nitrate is available in fertilizer form or as an industrial product. As such, its trade is not subject to special restrictions. And there are no controls on the sale of fuel oil, which, it is suspected, was mixed with ammonium nitrate to produce the Oklahoma bomb.

By contrast, the commercial blasting agent ANFO (ammonium nitrate-fuel oil) is strictly controlled. To buy it, one needs a license from the Bureau of Alcohol, Tobacco & Firearms, and records of transactions are scrupulously kept, says Thomas J. Dowling of the Institute of Makers of Explosives, Washington, D.C. And the Administration is seeking tighter controls on other explosive materials (see page 26).

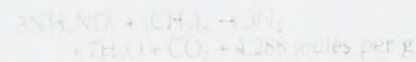
An ammonium nitrate bomb's power is clear from its reactions. Pure ammonium nitrate is stable. But at 251°C, it decomposes to produce gaseous products and heat:



At 300°C, different products and more energy are produced:



Combined with combustible material, such as fuel oil, the energy released increases almost tenfold:



Other likely bomb components, such as initiator materials, also are easy to acquire.

Reports suggest as much as 4,000 lb of an ammonium nitrate explosive in a rental truck were detonated in Oklahoma City. Edward E. Williams of the New Mexico Institute of Mining & Technology says the reported size of the bomb crater correlates with a 4,000-lb bomb. Controlled tests show that a 2,500-lb ANFO charge forms "a crater about 12 feet wide and 6 feet deep. Reports say the crater in Oklahoma City is about 20 feet wide and 8 feet deep," he says.

Depending on bomb size and distance from the blast, an explosion's effect on people and structures varies, Williams adds. People are killed and structures destroyed if hit directly by an overpressure of at least 20 psi. A 4,000-lb ANFO bomb produces this pressure up to 90 feet from the blast.

At the blast site, investigators are meticulously sifting through the rubble, gathering remnants of the bomb. They also will gather evidence such as fingerprints, hair, fibers, shoe prints, and tire treads.

The explosive can be identified by analyzing unreacted material, both ammonium nitrate and hydrocarbons from the fuel oil, notes Jay A. Siegel, professor of forensic science at Michigan State University, East Lansing. Analysis also will look for traces and breakdown products of other explosives that might have been used. Spot tests and screening by thin-layer chromatography or infrared spectroscopy likely will be performed in mobile labs near the site, with more detailed analyses at government labs.

Remnants of the device yield clues to involved terrorist groups and bomb component sources. The search for fragments will include X-rays of the dead, says forensic pathologist Michael M. Baden of the New York State Police. The painstaking process will take at least several months.

Maurice Rouhi

## National Academy of Sciences

Clayton H. Heathcock, professor of chemistry, UC Berkeley.

Robert Haber, head of department, Max Planck Institute for Biochemistry, Munich, Germany.

Dby Yeh, investigator, Howard Hughes Medical Institute, and professor of physiology and biochemistry, University of California, San Francisco.

Judith Kwik, investigator, Howard Hughes Medical Institute, and professor of biochemistry and molecular biology, University of Wisconsin, Madison.

Alexander M. Klibanov, professor of chemistry, Massachusetts Institute of Technology.

Stephen R. Leone, acting chief, quantum physics division, National Institute of Standards & Technology, and fellow, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder.

Edwin N. Lightfoot, professor of chemical engineering, University of Wisconsin, Madison.

Donald C. Malins, head, environmental biochemistry division, Pacific Northwest Research Foundation, Seattle.

Vincent Massey, professor of biological chemistry, University of Michigan, Ann Arbor.

Charles S. Parnetti, Distinguished Professor of Chemistry, Indiana University, Bloomington.

Gregory A. Petsko, Lucille P. Markey Professor, Rosenstiel Basic Medical Science Center, Brandeis University, Waltham, Mass.

Charles M. Radding, professor of human genetics and of molecular biophysics and biochemistry, School of Medicine, Yale University.

Stuart L. Schreiner, investigator, Howard Hughes Medical Institute, and professor of chemistry, Harvard University.

Douglas C. Wallace, professor of biochemistry, division of medical genetics, neurology and anthropology, and chairman, genetics and molecular medicine, School of Medicine, Emory University, Atlanta.

Carl E. Wieman, fellow, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder.

C&E NEWS 5/1/95



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