## PRACTICAL EMULSIONS

## PRACTICAL EMULSIONS

Volume II

## **Applications**

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## **Practical Emulsions, Applications, Volume II, 3<sup>rd</sup> Edition**

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#### **Foreword**

The first volume of *Practical Emulsions* has attempted to convey a general impression of the science of the formulation and manufacture of emulsions. Salient points have been presented in as simple a manner as possible, while detailed examination of specific points of the theory has been left to those whose qualifications and interests better fit them for such tasks.

In this volume, I have compiled basic formulations of many types of emulsion. This compilation is intended to provide graphic illustration of the breadth of emulsion technology. The formulations can also provide a starting point for the development of new and improved emulsion products and represent the types of product that can be made and their major constituents.

These formulations are provided by manufacturers to illustrate the use of their products. The suitability of any product for marketing, or the determination of the patent position regarding any formulation, is the responsibility of the person who manufactures and/or sells the product.

Many firms have generously provided formulation suggestions, and they merit my sincere appreciation for their help. Their contributions are acknowledged by appropriate references at the end of each chapter.

July 1967 J. L. Bishop, Jr.

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#### chapter 1

#### AGRICULTURAL EMULSIONS

The formulation of an agricultural emulsion requires unique considerations. The emulsion must possess sufficient stability to carry the active ingredient to the surface of the leaf, but must not allow re-emulsification of the active ingredients. The typical agricultural emulsion is comprised of a concentrate that contains the active ingredient (pesticide, herbicide, etc.), a surface-active agent, and a solvent. The emulsion is formed when the concentrate is mixed with water immediately prior to use. Therefore, the concentrate must immediately form an emulsion upon dilution with water.

The surfactant in a typical agricultural emulsion should provide an emulsion of small particle size. The surfactant should also aid wetting of the leaves by the spray. The surfactant can not permit re-emulsification of the spray on the leaf by rain water. Some investigators have found that anionic—nonionic blends of surfactants are more effective at a lower concentration and cost than unblended nonionic surfactants.¹ Cationic surfactants are often used as emulsifying and wetting agents in agricultural emulsions. If the spray contains a cationic rather than a nonionic wetting agent, more of the oil phase will be deposited on the leaves. The type and concentration of the cationic surfactant also influences the deposition of the oil phase on the leaves. Generally, the higher the efficiency of the emulsifying agent the lower the deposition of the oil phase on the leaf.²

A solvent is often found in the oil phase of an agricultural emulsion and is used to keep the active ingredients (pesticide, herbicide, etc.) and emulsifying agent in solution. The solvent should have a high flash point to avoid shipping restrictions.<sup>3</sup>

The adhesion of the oil-phase droplet to the leaf is affected by mechanical action as well as by the type and amount of surfactant and

solvent. The size of the droplet and its velocity affect the amount of the oil phase that will remain on the leaf. The evaporation rate of the emulsion is often lowered by the addition of saturated fatty acids to change the retention characteristics of the oil droplets.<sup>4</sup>

Agricultural sprays that are applied from low flying aircraft create special formulation problems. Aerial application of pesticides or herbicides is greatly affected by wind induced spray drifting. Although mechanical means of reducing drifting are occasionally used, most aerial agricultural sprays are water-in-oil emulsions rather oil-in-water emulsions. These "invert" emulsions form large droplets that are less affected by wind drifting.<sup>5</sup>

Aldrin Formulations	ns Chlordane Formulations		
Formula No. 16		No. 26	
Aldrin	26.8*	Chlordane	72.0
Xylene	31.6	Kerosene	20.0
Kerosene	31.6	Alkapent TD 100	3.0
Alkapent TD 100	4.0	Alkapent D NP 100	5.0
Alkapent D NP 100 2 lb/gal	6.0	8 lb/gal	
	N	o. 3 <sup>1</sup>	
		Soft water	Hard water
Chlordane		45.0	45.0
Triton X-151			1.3
Triton X-171		4.0	2.7
Kerosene 8.9 lb/gal		51.0	51.0
	DDT Fo	rmulations	
No. 48		Dowfax 9N9	5.0
DDT	25.0	Xylene	70.0
	No	o. 5 <sup>9</sup>	
		Soft water	Hard water
DDT		25.0	25.0
Triton X-151		0.9	2.5
Triton X-171		2.1	0.5
Xylene 8.0 lb/gal		72.0	72.0

<sup>\*</sup> Throughout this volume all figures are parts by weight, except where otherwise indicated.

Dieldrin Formulations		Dowfax 9N9	5.0
No. 6 <sup>10</sup>		Kerosene	75.0
Dieldrin	20.0	No. 9 <sup>13</sup>	
Dowfax 9N9	5.0		20.0
Xylene	75.0	Lindane Emulsifier C	20.0
*	75.0		7.5 32.5
No. 7 <sup>11</sup>	10.0	Velsicol AR-50	
Dieldrin	19.0	Isophorone	40.0
Heavy aromatic Naphtha	77.0	No. 10 <sup>14</sup>	
Alkapent TD 100	4.0	Malathion Wettable	
Alkapent D NP 100	6.0	Malathion (97% active	
1.5 lb/gal		Celite 209	28.7
Lindane Formulations		Barden clay	42.5
No. 8 <sup>12</sup>		Sodium lignosulfonate	2.0
Lindane	20.0	Dowfax 9N9	1.0
_	No	1115	
М		n-Xylene	
142			Hard water
Malathion (95%)	•	52.7	52.7
Triton X-152		3217	4.0
Triton X-172	5.0 1.0		
Xylene	-11		42.3
8.6 lb/gal			
No. 12 <sup>16</sup>		No. 14 <sup>17</sup>	
Methyl Parathion Emuls	ion	Toxaphene Formu	ulation
Concentrate	1011	Toxaphene	60.0
Technical Methyl Parathion	31.40	Dowfax 9N9	5.0
Xylene	63.60	Kerosene	35.0
Atlox 3335	4.25	No. 15 <sup>17</sup>	
Atlox 8916P	0.75		mmulatian
8.05 lb/gal	0.75	Toxaphene-DDT For	40.0
		Toxaphene DDT	20.0
No. 13 <sup>17</sup>		Dowfax 9N9	5.0
Ronnel Formulation		Xylene	35.0
0, 0-Dimethyl, 0-2, 4, 5-			The state of the s
Tricholrophenyl Phos-	• 4 0	2, 4-D Formula	tions
phorothioate (Ronnel)	24.0	No. 16 <sup>17</sup>	
Dowfax 9N9	2.5	Isooctyl Ester of 2	
Petroleum Sulfonate	2.5	Formulation	
Xylene	71.0	Isooctyl Ester of 2, 4-	D 65.0

Danifor ONO	2.2		
Dowfax 9N9 Petroleum Sulfonate	1.8		
Heavy Aromatic Naphtha	31.0		
No. 17 <sup>17</sup>			2.4
Butyl Ester of 2, 4-D	)	Dowfax 9N9	2.4
Formulations		Petroleum Sulfonate	1.6
Butyl Ester of 2, 4-D	56.0	Heavy Aromatic Nap	htha 40.0
	No.	1818	
	S	oft water	Hard water
2,4-D Butyl Ester		57.0	57.0
Triton X-152		0.6	2.0
Triton X-172		3.4	2.0
HAN-132		39.0	39.0
8.95 lb/gal		•	
		1918	
	2,4,5-T	Isooctyl Ester	
	S	oft water	Hard water
2,4,5-T Isooctyl Ester		65.8	65.8
Triton X-152		0.4	1.6
Triton X-172		3.6	2.4
Diesel Oil		30.2	30.2
8.82 lb/gal			
No. 20 <sup>19</sup>		Shellac	100
2-Ethylhexyl-2, 4, 5-	-	Water	2000
Trichlorophenoxyaceta	ate	Dilute before use	
2-Ethylhexyl-2, 4, 5-Trich-		No. 22 <sup>21</sup>	
lorophenoxyacetate	64.2	Paraffin Wax	553
Monazoline O	5.3	Carnauba Wax	68
Monapal T	2.7	Cottonseed Oil	98
Xylene	27.8	Oleic Acid	183
		Triethanolamine	98
Fruit Coating Wax		Water (containing Soc	da Ash) q.s.
Emulsions		No. 23 <sup>22</sup>	
No. 2120		Paraffin Wax	168.0
Caustic Soda	6	Beeswax	42.0
Triethanolamine	20	Oleic Acid	22.0
Stearic Acid	42	Sodium Bicarbonate	6.6
Paraffin Wax	165	Salt	2.2
Carnauba Wax	55	Water	599.2

CATTLE DIPS		XA	27.4
Toxaphene Formulat	ions	Atlox 3404	6.0
No. 24 <sup>23</sup>		Atlox 3403	9.0
Toxaphene (90%)	66.6	No. 27 <sup>23</sup>	_
Kerosene	18.4	Soil Fumigant*	k
Atlox 3404	6.0	Nemogon® (3)	83.7
Atlox 3403	9.0	Xylene (b)	11.3
No. 25 <sup>23</sup>		Atlox 3404	1.0
Toxaphene (90%)	55.3	Atlox 3403	4.0
Malathion (95%)	5.3	No. 28 <sup>23</sup>	
XA	24.1	Miticide*	
Atlox 3404	6.0	Aramite (93%)	91.0
Atlox 3403	9.0	XA	2.0
No. 26 <sup>23</sup>		Atlox 3409	7.0
Toxaphene (90%)	55.6	* For longer shelf life,	add 0.5%
Lindane	2.0	Epichlorhydrin to these for	

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#### chapter 2

#### **BITUMINOUS EMULSIONS**

Bituminous emulsions are generally used as surface coatings. These emulsions are used in addition to fibers for protection of roads and highways. They are characterized by a low concentration of a relatively inexpensive surfactant.

Cationic surfactants are used for bituminous emulsions. The cationic material is strongly adsorbed at negatively-charged mineral surfaces. The mineral surface becomes water repellent because of the adsorbed cationic surfactant. The bitumen will adhere better to this water repellent surface and therefore can more effectively fulfill its purpose of holding together the mineral particles in the road surface. Thus, the cationic surfactants are often referred to as adhesion promoters. In use, the cationic bitumen-in-water emulsion is applied to the stone road surface. It breaks upon contact with the road surface and the bitumen follows the cationic surfactant to adhere to the stone surface, while the water runs away.<sup>22</sup>

Various anionic surfactants are also used for surface dressing of roads. Based upon the bitumen, 0.5 to 2.5% surfactant is added to asphalt and tar macadam basecourses and fine cold asphalt to protect the binder-to-stone bond from water action. Britain and Sweden make use of this technique to prevent stripping of oiled gravel surfaces, in addition to the above road surfaces.<sup>23</sup>

Asphalt Emulsions		Green Acid Soap (Dry	
Formula No. 1 <sup>1</sup>		<b>Basis</b> ) 0.23	
Asphalt	64.05	The asphalt for use in this	
Water	35.00	formula may be produced from	
Caustic Soda	0.08	Mid-Continent petroleum, melt-	
Corn Gluten (or Soya		ing point about 110°F, penetra-	
Bean Meal)	0.64	tion about 130 at 77°F.	

Green acid soap may be prepared by the neutralization of green acids, which are well known in the petroleum industry. If the green acid soap contains appreciable amounts of oil, a harder asphalt should be emulsified to produce a residue of given penetration.

The caustic, farinacious emulsifier, and green acid soap are mixed with water and heated to a temperature of about 200°F. This hot solution or mixture is placed in a suitable stirrer, agitator, or mixer and is beaten by paddles, circulated by centrifugal pumps, or dispersed between suitable rotors moving at high velocities.

The melted asphalt at about the same temperature is slowly stirred into the solution and further agitated until complete emulsification has taken place. When high melting point asphalts are used, it may be necessary to increase the temperature at which the asphalt is added, but it is desirable to keep the temperature of the emulsion below the boiling point of water so that the foaming due to the production of steam may be prevented.

No. 22

A sodium oleate solution is made up to a concentration of 20% by the addition of oleic acid and caustic soda to water at 90°C. This is then diluted with

nine times its volume of water heated to 90°C. The 2% soap solution is run through a colloid mill with an equal amount of asphalt heated to a temperature not exceeding 100°C. The resultant emulsion contains equal parts of asphalt and water with 1% by weight of soap.

No. 33

A hot dilute aqueous solution of alkali, such as a solution of caustic soda of about 0.5% strength, is prepared. An approximately equal weight of asphalt is melted; part of the melted asphalt is slowly stirred into the hot solution until scum begins to form on the surface; then a small quantity (about 0.5% of the final product) of oleic acid is added, followed by addition of the rest of the asphalt, while the temperature and agitation are maintained and a small proportion of clay added to give desired stability and adhesiveness.

	No. 44	
A.	Rosin	100
	Slaked Lime	${100 \atop 3\frac{3}{4} \atop 103}$ C
B.	Fuel Oil	103 J

Heat A at 140°C and mix until uniform. Add B while mixing. Take 4 lb of C and add to 100 lb of melted bitumen or asphalt. Disperse the mixture in 0.05 N potassium rosinate solution to give a 57% bitumen

content.	
No. 5 <sup>5</sup>	
Asphalt	48-52
Water	46-48
Oleic Acid	1
Sodium Hydroxide	<1
Bentonite	1
No. 66	

Nine parts of soap are dissolved in 78 parts of warm water. About 20 parts of a low-grade fuel oil or a crude oil with an asphaltic base are added slowly, with vigorous agitation.

No. 7 <sup>7</sup>	
Asphalt	500
Water	500
Bentonite	30
Quebracho	30
Soda Ash	10

The bentonite, quebracho, soda ash, and water are mixed and heated to 200°F. While stirring, the asphalt, which has been heated to approximately 200°F, is added. The stirring is continued until the asphalt is dispersed.

No. 88	
Asphalt	2800
Water	2800
Rosin Soap (50%)	118
Pine Oil	40

The rosin soap is added to the water and is heated to 200°F. The asphalt is also heated to 200°F and the pine oil added. While agitating, the asphalt is slowly poured into the water.

The mixture is agitated until a smooth emulsion is formed.

omooth omasion to retime.
No. 99
Hydrous Magnesium
Silicate 8-10 lb
Water 20 gal
Mix well and heat to boiling;
then mix in an emulsifying ma-
chine with
Asphalt, melted 36 gal
Acetic Acid
(0.1 N) 250-240 cc
Water, boiling 10 gal
No. 10 <sup>10</sup>
Adhesive for Sound-Deadening

## Adhesive for Sound-Deadening Pads

	****
Asphalt	50-60
Bentonite	2-3
Oxalic Acid	0.02
Kerosene	3-10
Water	To make 100

The asphalt is warmed in the kerosene until dissolved. The bentonite and oxalic acid are dissolved in water and heated to boiling. The solutions are vigorously mixed and run through a colloid mill, if necessary.

# No. 11<sup>11</sup> Millboard Adhesive Asphalt 100 Tall Oil Soap (50 % water) 30 Kaolin 30

The tall oil soap and kaolin are mixed while heating and the molten asphalt slowly added, with stirring.

Before use, hot water in the desired quantity is added.

No. 12 <sup>12</sup>		
Soft Asphalt Emulsion		
Water	400	
Carbopol 941	1.5 (0.19%)	
Sodium hydroxide	(10%	
solution)	4.5	
Ethomeen C-25	0.75	
Soft Asphalt*	400	

\* Sohio 180-200 asphalt, Standard Oil Co. of Ohio, Cleveland, Ohio.

Carefully disperse the Carbopol 941 in the water. After thorough dispersion, neutralize with the sodium hydroxide followed by addition of the Ethomeen C-25. Heat this mucilage to 65-70°C. (The water can be heated prior to the addition of the Carbopol 941 and neutralizer as this will assist dispersion of the Carbopol 941.) Separately heat the asphalt to 85°C. Utilizing moderately high shear mixing, slowly add the molten asphalt to the water mucilage. Add the asphalt no faster than the rate of dispersion. If the asphalt is added too rapidly, the emulsion will invert and separate.

When the asphalt has been added, continue mixing for a short time to insure uniformity. Shock cool the emulsion without mixing and allow it to remain undisturbed until its temperature falls to 30-35°C.

٠		No. 13 <sup>13</sup>	No.14 <sup>13</sup>
A.	Asphalt†	65	65
В.	Water	35	35
C.	Diam 26	0.1-0.2	
	Diam 11-C		0.25-0.30
D.	Conc. Hydrochloric Acid††	0.05-0.15	0.15-0.20

For optimum stability and minimum processing costs, the emulsion should be formed inside a colloid mill with the water and asphalt fed to the mill separately. Two methods of accomplishing this follow. The first method leads to somewhat better emulsions but requires HCl-resistant processing equipment. The amine salt used in Method II is noncorrosive.

#### METHOD I

- (1) Dilute D in B
- (2) Add C to A. The asphalt and water should be in separate tanks and independently connected to the mill through pumps.

<sup>† 150-200</sup> or 200-250 penetration paving grade asphalt, 60 to 70 parts of asphalt, may be used provided the emulsifying agent concentration is adjusted to correspond.

<sup>††</sup> pH is usually adjusted to 6.0-6.5.

(3) Simultaneously pump AC and BD into the colloid mill, at a proportion of 65/35.

#### METHOD II

- (1) Melt C and add a portion of the water; finally, add D.
- (2) Recycle with the pump to emulsify CD.
- (3) Pump BCD into another tank containing the remainder of the water, agitate or recirculate.
- (4) Heat BCD to 80-90°C and the asphalt to 115-120°C.
- (5) Pump the asphalt and BCD into the colloid mill in proportions of 65/35.

#### No. 1514

1000 g of bitumen (preferably asphalt) are heated to 90°C. 60 g of Swedish resin at 80-90°C are then added, and finally, a solution of 20 g of caustic potash in 120 g of water, cooled to 60-70°C. Vigorous stirring is needed throughout. 1000 g of hot water are poured in and when soap formation is ended, 800 g of water are added.

#### No. 1615

Add 15 parts by weight of oleic acid to 250 parts by weight of asphalt flux oil, heating the mix to about 100°C. Add this to 750 parts of water to which have been added 34 parts of aqueous ammonia, to form an emulsion of the asphalt flux oil, which has a greater viscosity substantially than that of water. Add 1500 parts by weight of coal tar, specific gravity of about 1.18 or more, heated to a temperature of about 70°C, to which has been added 45 parts of oleic acid. Vigorously agitate the tar with the emulsion of asphalt flux oil and subject the resulting mixed emulsion to intensive mechanical disintegration—for example, by passage through a colloid mill.

#### No. 1716

Emulsion for road making
Spramex Bitumen 48.0
Water 49.5
Sodium Carbonate (calcined) 0.5
Oleic Acid 2.0

The bitumen is warmed at 95-98°C and the oleic acid added. The water is heated separately with the sodium carbonate and the two liquids are introduced into the emulsifier.

No. 18 <sup>16</sup>	
Spramex Bitumen	50.0
Mineral Oil	2-2.5
Resin Soap	1.5-2.0
Caustic Potash	1.0
Water	45.0
TT1 1	

The bitumen is melted and the mineral oil added during agitation. The water is heated to boiling and in it are dissolved the soap and the caustic potash. The liquids are mixed at 95°C. With more bitumen, 1-2% of blue starch, gelatin, or sodium silicate must be added during or after emulsification.

#### No. 1917

Melt 100 parts of bitumen, softening point 45-50°C, and add 10.8 parts of rosin; heat to 100-125°C. Then add 20 parts of kaolin (soaked in equal parts by weight with water) and 1.2 parts of sodium hydroxide, preheated to 70-80°C. Raise the temperature of this mixture to 100°C and dilute with water to produce an emulsion containing 20-25% solids.

No. 2018	
Bitumen	35
Coal, powdered	15
Carragheen	1
Water	50
,	

	,	
	No. 21 <sup>19</sup>	
	Pitch Emulsion	
A.	Coal Tar Pitch	180
	Stearin Pitch	20
В.	Casein Solution*	45
	Water	35
	Caustic Potash	1
C.	Water, boiling	120
	Melt A together and add	to B
at 1	100°C. Add C.	

* Casein Solution	
Casein	56
Caustic Potash (50%)	10
Water	494
Cresylic Acid	11

#### Tar Asphalt Emulsion No. 22<sup>20</sup>

Shale Tar	38.15
Water	49.60
Mexican Asphalt	7.63
Casein	1.15
Rosin	1.15
Potato Starch	0.76
Anthracene Oil	1.34

#### Tar Emulsions

No	. 23	21
No	. 23	۲

Wa	ter	50.000
RT	-12 tar	50.000
Car	bopol 941	0.125
A.	Sodium hydroxide	
	(10% solution)	0.375
	Ethomeen C-25	0.625

Carefully disperse the Carbopol 941 in the water in a jacketed vessel, and add A. Heat both the water mucilage and the tar to 65°C. Slowly add the molten tar to the hot mucilage with vigorous mixing (a mixer such as a medium-speed Eppenbach homogenizer is recommended). After the last of the tar has been added, mix briefly to ensure homogeneity. Rapidly cool the emulsion without further mixing.

The mixing step is critical. With very high shear mixing, the tar particles are extremely small and the emulsions are very smooth. Films deposited from such emulsions are difficult to dry, however, because an impermeable layer forms on the top. In contrast, emulsions formed with moderate shear have rela-

tively large tar particles but dry evenly and rapidly.

No. 24 <sup>21</sup>	
Water	50.000
RT-8 tar	50.000
Carbopol 941	0.125
Sodium hydroxide	
(10% solution)	0.250
Ethomeen C-25	0.063
Carefully disperse the	Carbo-

Carefully disperse the Carbopol 941 in the water. When dispersion is complete, add the sodium hydroxide and then the amine. Lastly, slowly add the RT-8 tar in a thin, continuous stream (so that the rate of addition is no greater than the rate of dispersion) with good mixing. Fairly high shear, such as that provided by a medium-speed Eppenbach homogenizer, forms the best (smallest droplet-size) emulsion. Excessively rapid addition of the tar results in a grainy emulsion.

No. 25 <sup>21</sup>	
Creosote Emulsion	
Water	200.00
Carbopol 934	0.60
Sodium Hydroxide	
(10% solution)	0.55
Creosote	200.00
Carefully disperse the	Carno-

Carefully disperse the Carpopol in the water and add the sodium hydroxide. Add the creosote in a slow stream while vigorously agitating the mix. Stir to uniformity.

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- 2. Air Reduction Co., Inc.
- 3. Alabama Binder and Chemical Corp.
- 4. Alco Chemical Co.
- 5. Alcolac Chemical Corp.
- 6. Amalgamated Chemical Corp.
- 7. American Can Co., Marathon Products Division
- 8. American Cholesterol Products. Inc.
- 9. American Cyanamid Co.
- 10. American Dyewood, Inc.
- 11. American Lecithin Co.
- 12. Amoco Chemicals Corp.
- 13. Apex Chemical Co., Inc.
- 14. Archer Daniels Midland Co.
- 15. Ardmore Chemical
- 16. Arizona Chemical Co.
- 17. Arlen Chemical
- 18. Armour Industrial Chemical Co.
- 19. Arol Chemical Products
- 20. Atlas Chemical Industries, Inc.
- 21. Atlas Refinery, Inc.
- 22. Baker Castor Oil Co.
- 23. Barrett Chemical
- 24. BASF Colors and Chemicals, Inc.

- 25. Beacon Chemical Industries, Inc.
- Berkshire Color and Chemical Co.
- 27. Boler Petroleum Co.
- 28. Burkart Schier Chemical Co.
- 29. Bryant Chemical
- 30. Bryton Chemical Co.
- 31. Calgon Corp.
- 32. California Chemical Co.
- 33. Canada Packers Ltd.
- 34. Cargill, Inc.
- 35. Chemical Corp.
- 36. Carlisle Chemical Works, Inc.
- 37. Central Soya Co.
- 38. Chapman Chemical Co.
- 39. Chemactants, Inc.
- 40. Ciba Chemical and Dye Co., Inc.
- 41. Cindet Chemicals, Inc.
- 42. Clintwood Chemical Co.
- 43. Clough Chemical Co., Ltd.
- 44. Colgate-Palmolive Co.
- 45. Colloidal Products Corp.
- 46. Colloids, Inc.
- 47. Colonial Sugars Co.
- 48. Commercial Solvents Corp.
- 49. Continental Chemical Co.
- 50. Crest Chemical Corp.

- 51. Croda, Inc.
- 52. Crown Chemical Corp.
- 53. Crown Zellerbach Corp.
- 54. Culver Chemical Co.
- 55. DePaul Chemical Co.
- 56. Dexter Chemical Corp.
- 57. Diamond Alkali Co.
- 58. Distillation Products Industries
- 59. Dixo Company, Inc.
- 60. C. B. Dolge Co.
- 61. Dominion Products, Inc.
- 62. The Dow Chemical Co.
- 63. Drew Chemical Corp.
- 64. DuBois Chemicals, Inc.
- 65. E. I. du Pont de Nemours and Co.
- 66. Eastern Color and Chemical Co.
- 67. Emery Industries, Inc.
- 68. Emkay Chemical Co.
- 69. Essential Chemicals Corp.
- 70. W. F. Fancourt Co.
- 71. Far-Best Corp.
- 72. Fine Laboratories, Inc.
- 73. Fine Organics, Inc.
- 74. Finetex, Inc.
- 75. R. E. Flatow and Co., Inc.
- 76. Foremost Chemical Products Co.
- 77. Geigy Industrial Chemicals
- 78. General Aniline and Film Cerp.
- 79. General Mills
- 80. Georgia-Pacific Corp.
- 81. Goldschmidt Chemical Corp.
- 82. Glidden Co.
- 83. Glyco Chemicals, Inc.
- 84. B. F. Goodrich Chemical

Co.

- 85. Greenwood Textile Supply Co.
- 86. Guardian Chemical Corp.
- 87. C. P. Hall Co.
- 88. Hart Products Corp.
- 89. Henkel International Gmbh, A. H. Carnes Co., agent
- 90. Hercules Powder Co.
- 91. Hexagon Laboratories Inc.
- 92. Hodag Chemical Corp.
- 93. Hooker Chemical Corp.
- 94. Hope Chemical
- 95. E. F. Houghton and Co.
- 96. Humble Oil and Refining Co.
- 97. I. C. I. Organics, Inc.
- 98. International Selling
- 99. Intex Chemical Corp.
- 100. Ion acChemical Co.
- 101. Isochem Corp.
- 102. Jefferson Chemical Co.
- 103. Andrew Jergens
- 104. Jersey State Chemicals
- 105. W. H. and F. Jordan, Jr., Mfg. Co.
- 106. Kali Mfg. Co.
- 107. Kalide Corp.
- 108. Kehew-Gradley and Co.
- 109. Kessler Chemical Co., Inc.
- 110. Knapp Products, Inc.
- 111. H. Kohnstamm and Co.
- 112. Laurel Soap Mfg.
- 113. Leatex Chemical Co.
- 114. Lever Brothers Co.
- 115. Levda Oil and Chemical Co.
- 116. Maher Color and Chemical Co.
- 117. Malmstrom Color and

- Chemical Corp.
- 118. Marden-Wild Corp.
- 119. Mathe Chemical Co.
- 120. Merix Chemical Co.
- 121. Metro-Atlantic, Inc.
- 122. M. Michel and Co.
- 123. Harry Miller Corp.
- 124. 3M Company
- 125. Miranol Chemical Co., Inc.
- 126. Mona Industries, Inc.
- 127. Monsanto Chemical Co.
- 128. Moretex Chemical Products
- 129. Murphy-Phoenix Oil Co.
- 130. National Lead Co.
- 131. Nopco Chemical Co.
- 132. Northwestern Chemical Co.
- 133. Nostrip Chemical Works, Inc.
- 134. Onyx Chemical Corp.
- 135. Ottol Oil Co.
- 136. Patent Chemicals
- 137. Pecks Products, Co.
- 138. Pennsalt Chemicals Corp.
- 139. Pennsylvania Refining Co.
- 140. Perry Brothers, Inc.
- 141. Pilot Chemical Co.
- 142. Charles Pfizer and Co.
- 143. Pro-Chem. Inc.
- 144. Proctor and Gamble, Co.
- 145. Proctor Chemical Co.
- 146. Proven Products
- 147. Rohm and Haas Co.
- 148. Relly-Whiteman-Walton Co.
- 149. Retzloff Chemical Co.
- 150. Richardson Co.
- 151. Robeco Chemicals, Inc.
- 152. Robinson Wagner Co., Inc.
- 153. Rozilda Laboratories
- 154. Ryco, Inc.
- 155. Sher Brothers

- 156. Scholler Brothers, Inc.
- 157. Seaboard Chemicals, Inc.
- 158. Shawinigan Resins Corp.
- 159. Shell Oil Co.
- 160. George F. Siddall, Co.
- 161. Werner G. Smith, Inc.
- 162. Sole Chemical Corp.
- 163. Solvol Chemical Co., Inc.
- 164. Sonneborn Chemical and Refining
- 165. Southern Sizing Co.
- 166. Fredrick A. Stresen-Reuter, Inc.
- 167. A. E. Staley Manufacturing Co.
- 168. Standard Chemical Co.
- 169. Standard Chemical Products
- 170. Stauffer Chemical Co.
- 171. Stepan Chemical Co.
- 172. Sun Chemical Corp.
- 173. Suffact Co., Inc.
- 174. Swift and Co.
- 175. Synthetic Chemicals, Inc.
- 176. Synthron, Inc.
- 177. Tanatex Chemical Corp.
- 178. Textilana Corp.
- 179. Textron, Inc.
- 180. Thompson Chemical Corp.
- 181. Thompson-Hayward Chemical Co.
- 182. Titan Chemical Products, Inc.
- 183. Arthur C. Trask Co.
- 184. Treplow Chemicals, Inc.
- 185. Trylon Chemicals, Inc.
- 186. Union Carbide Corporation (Chemicals and Silicones Divisions)
- 187. United Merchants and

Manufacturers, Inc.

- 188. Universal Chemicals Corp.
- 189. Van Dyk and Co.
- 190. Varney Chemical Corp.
- 191. Verona-Pharma Chemical Corp.
- 192. Wasco Laboratories
- 193. Washine Chemical Corp.
- 194. Wayland Chemical Corp.
- 195. Wilson and Co., Inc.
- 196. Witco Chemical Co., Inc.

- 197. W. A. Wood, Co.
- 198. Woonsocket Color and Chemical Co.
- 199. Wyandotte Chemicals Corp.
- 200. General Electric Silicones
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- 201. Dow Corning Corp.
- 202. Allied Chemical Corp, National Aniline Division
- 203. Chevron Chemical Co., Oronite Division
- 204. Tennessee Corp.

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