Polyamides From Polymeric Fat Acids

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FOR the past several years the Oil and Protein division of the Northern Regional Research Laboratory has been engaged in an investigation of the polymerization phenomena of drying and semi-drying oils with the object of developing new and useful industrial applications of these oils. Certain phases of this research culminated in the development of Norepol (7), a rubber replacement, and in the preparation of improved synthetic drying oils (8).

Another approach to the problem has led to synthesis of polyamides from polymeric fat acids. One of these, the polyamide of ethylene diamine and polymeric fat acids, has recently been introduced to the protective coating and packaging industries as "Norelac"[3] (10, 11). The present paper reports on the preparation and properties of a series of polyamides obtained by reaction of polymeric fat acids with a variety of difunctional and polyfunctional amines.

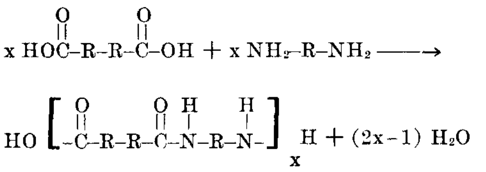
Laboratory preparation of methyl esters of polymeric fat acids has been described by Bradley and Johnston (3). They polymerized methyl esters of fat acids derived from soybean, linseed, tung, and other oils and isolated the polymerized products by means of vacuum distillation of the unpolymerized monomers. In another paper Bradley and Johnston (4) reported separation by means of molecular distillation of dimers and trimers from polymers obtained by heating methyl esters of dehydrated castor oil fat acids.

The results of Bradley and Johnston indicated that these dimeric and trimeric fat acid esters were derived from polymerization of polyunsaturated acids such as linoleic, linolenic, and eleostearic acids found in soybean, linseed, tung, and dehydrated castor oils. These dimeric and trimeric fat acids were shown to be dibasic and tribasic acids, respectively.

Dimeric and trimeric fat acid esters are believed (4) to be formed by a condensation similar to that undergone by butadiene in its polymerization to vinyl cyclohexene and octahydrodiphenyl. Barbot (2) has presented evidence that he has converted dimeric fat acid esters into a derivative of an aromatic hydrocarbon, probably benzene.

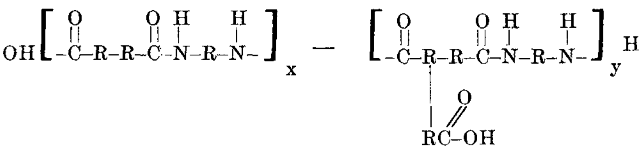
Previous work at this laboratory led to a procedure for the semicommercial production of polymeric fat acids from vegetable oils (7). The oil is converted to its methyl esters by methanolysis and excess methanol and glycerol are recovered. The methyl esters are then heat polymerized, and the product is subjected to vacuum and steam distillation to remove unpolymerized esters. The polymeric fat acids are obtained by saponification of the polymerized esters and subsequent neutralization.

A typical polycondensation reaction of a dibasic acid with a diamine to form a linear polyamide is shown by the following equation:



$$x\,HO\overset{O}{\overset{\|}{C}}-R-R-\overset{O}{\overset{\|}{C}}-OH + x\,NH_2-R-NH_2 \longrightarrow HO\left[-\overset{O}{\overset{\|}{C}}-R-R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\right]_x H + (2x-1)\,H_2O$$

Since the polymeric fat acids are a mixture of dibasic and tribasic acids the polycondensation would yield, in the earlier stages, a polyamide having a structure similar to the following:



I.

Actually the dibasic and tribasic acid residues would not be segregated, as shown in the formula, but would be distributed along the chain in a manner dependent upon the ratio of x to y and the laws of probability. Because of the remaining carboxyl group in each tribasic acid residue, cross-linking will occur in later stages of the polycondensation, and a gelled, i.e., infusible and insoluble, product will result. However, owing to the rather high molecular weight of the dibasic and tribasic fat acids (580 and 870, respectively), a high degree of reaction (5) is not required to produce a polymer having a molecular weight of 3,000-5,000. Furthermore, the reaction may readily be controlled so that gelation will not occur unless deliberate attempts are made to drive the condensation to completion. Since polyamides of polymeric fat acids contain carbon-to-carbon unsaturation, gelation may also be effected by oxygen; consequently, all polycondensations were conducted under an inert atmosphere.

IF polymeric fat acids are condensed with amines of the polyethylene polyamine series, the polyamides produced gel very readily. It is possible, however, to control gelation and to obtain satisfactory polyamides if a functionality of 2 is assumed for the polyamines and is used in calculating the equivalent amounts of polymeric fat acid and polyamine. Successful reaction under these conditions follows from the theoretical considerations of Flory (13) on the relationship of functionality and excess of reagent to gelation. Further reference to this relationship is made later.

Another possibility of interest in the preparation of polyamides of polymeric fat acids is that of modification with monofunctional acids and amines. The situation is analogous to that existing in the prepara-

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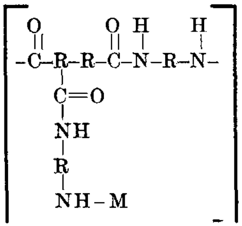
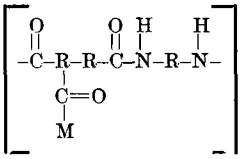
[3] From NOrthern REgional LACquer.

tion of modified glycerol phthalate polymers. Thus, macro-molecules containing units such as those in formulas II and III, where M represents a monofunctional radical, can be obtained.



II.



III.

The presence during condensation of the monofunctional reactant greatly reduces the possibility of cross-linking, and for this reason the modified polyamides are more difficult to gel than the unmodified. This effect is similar to that of an excess of difunctional reactant, although the molecular weight of a modified polyamide will exceed that of a polyamide containing an excess of difunctional reagent.

Experimental Part

Materials. The origin and purity of materials used in this investigation are summarized in Table I.

Preparation of the Nitrile of Dimeric Fat Acids. A procedure similar to that described by Ralston, Pool, and Harwood (15) was followed. Anhydrous ammonia was passed into polymeric soybean fat acids (acid value 195) at 150°-160° C. for 15 hours. The temperature was then increased to 280°-300° for 6 hours. The final acid value was 0.86. The material was distilled at 1 mm. pressure, and the distillate boiling at 268°-309° C. ($n_d^{30} = 1.4898$) was collected. The yield was 50 per cent of theoretical. *Anal.* Calcd. for $C_{34}H_{62}(CN)_2$: N, 5.36. Found: N, 5.35.

Reduction of Nitrile to Diamine. Reduction was accomplished by the method of Sutter and Moffet (16). The diamine was obtained in 40 per cent yields as a yellow oil. *Anal.* Calcd. for $C_{36}H_{66}(NH_2)_2$: N. E. = 265; Found: N. E. = 319. It was not possible to purify the product, and the crude diamine was therefore used in subsequent reactions.

Preparation of Monostearoyl Ethylene Diamine. This material was obtained by a modification of the procedure of Aspinall (1). One mole of commercial methyl stearate was refluxed 10 hours with 2 moles of an aqueous (69.5 per cent) solution of ethylene diamine. After volatile material was removed by distillation at reduced pressure, the residue consisted of a mixture of mono- and distearoyl ethylene diamine with some unreacted methyl stearate. Distearoyl ethylene diamine was removed by crystallization of the mixture from ethanol in which the distearoyl derivative is sparingly soluble. Evaporation of the mother liquors left monostearoyl ethylene diamine contaminated with a little methyl stearate. The yield of a waxy solid of indefinite melting point was 50-65 per cent of theoretical. *Anal.* Calcd. for $C_{20}H_{42}ON_2$: N. E. = 326; Found: N. E. = 351. No purification could be effected by recrystallization from ethyl acetate.

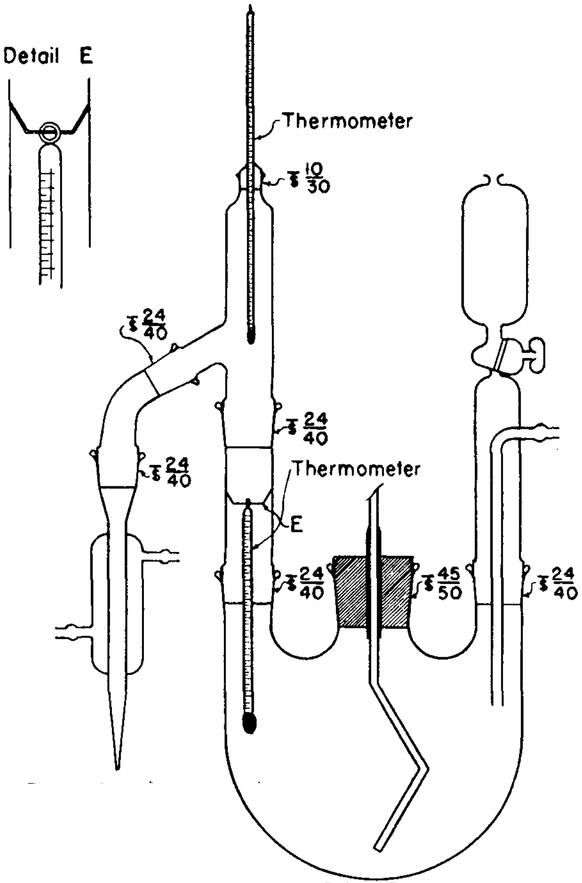


FIG. 1. Reaction Vessel.

Preparation of Polyamides. Laboratory preparation of polyamides from polymeric fat acids was

TABLE I.

Materials Used in Preparation of Polyamides.

Name	Source	Grade and remarks
Polymeric soybean fat acids	W. G. Smith Company	Neutralization equivalent = 296; dimer-trimer ratio 1.83[1]
Polymeric soybean fat esters	Northern Regional Research Laboratory	Sapon. equivalent = 298; dimer-trimer ratio 1.99[1]
Polymeric linseed fat esters	Northern Regional Research Laboratory	Sapon. equivalent = 330; dimer-trimer ratio 0.88[1]
Monomeric fat acids	Northern Regional Research Laboratory	Distilled. Obtained from recovered unpolymerized soybean methyl esters
Abietic acid	Hercules Powder Company	Rosin, Grade K; N. E. = 351
Benzoic acid	Eastman Kodak Company	Reagent
Maleic acid	Eastman Kodak Company	Reagent
Naphthenic acid	Eastman Kodak Company	Practical; N. E. = 210
Sebacic acid	Eastman Kodak Company	Reagent
Stearic acid	Eastman Kodak Company	Reagent
Ethylene diamine	Carbide and Carbon Chem. Corp.	Commercial, 70 per cent solution
Propylene diamine	Eastman Kodak Company	Practical, 80-85 per cent solution
Diethylene triamine	Carbide and Carbon Chem. Corp.	Commercial
Triethylene tetramine	Carbide and Carbon Chem. Corp.	Commercial
Hexamethylene diamine	E. I. duPont de Nemours and Co.	Commercial
Hydrazine hydrate	Eastman Kodak Company	Reagent
n-Dodecyl amine	Armour and Company	Purified; N. E. = 191
Monostearoyl ethylene diamine	Northern Regional Research Laboratory	See experimental; N. E. = 251
Diamine from dimeric fat-acid	Northern Regional Research Laboratory	See experimental; N. E. = 319

[1] Assayed by the method of Cowan, Falkenburg, and Teeter (9).

effected by placing 500 g. of acid in a 3-liter, 3-necked flask fitted with a dropping funnel, a stirrer, thermometer, inlet tube for nitrogen, and a distilling head with condenser for removal of water formed during the reaction (Figure 1). The acid was heated to 150° C., and an equivalent quantity of the polyamine or its aqueous solution was slowly added dropwise over a period of 45-60 minutes. The resulting mixture was slowly heated over a period of about 1½-2 hours to a temperature of 200° C. Then the system was placed under reduced pressure (10-15 mm.) for 15 minutes at 200° C. Nitrogen was admitted to the reaction vessel, and heating at 200° C. was continued at atmospheric pressure until the gel time had fallen to about 10-30 seconds. The product was then poured into a suitable container and kept under an inert atmosphere until cool.

Essentially the same procedure was followed when polyamides were prepared by aminolysis of polymeric fat acid esters except that all the polyamine was added at once. The mixture was then heated at 120°-150° C., and the water and methanol were removed by distillation. Distillation was continued until most of the theoretical amount of volatile substances had been collected before increasing the temperature to 200° C. In the case of ethylene and propylene diamines it was advantageous to utilize a small fractionating column in order to facilitate separation of water and methanol from the reaction mixture and to minimize losses of diamine.

Preparation of Copolyamides and Modified Polyamides. Copolyamides were prepared by mixing the desired amount of maleic or sebacic acid with polymeric fat acids and then condensing the mixture with ethylene diamine by the foregoing procedure or by allowing polymeric fat acids to react with a mixture of polyamines.

Modified polyamides of two types were synthesized. One type was prepared by condensing ethylene diamine with a mixture of polymeric fat acids and various monobasic acids. The second type was prepared by condensing mixtures of ethylene diamine and monofunctional amines with polymeric fat acids. When monobasic acid was used, it replaced polymeric fat acids to the extent of 10 per cent of the total equivalents of carboxyl. When monofunctional amine was used, it replaced ethylene diamine in an amount equivalent to one-third of the total trimeric acid carboxyls present in the polymeric fat acids.

Determination of Extent of Reaction. During polyamide preparations the progress of the reaction was easily followed by noting the amount of distillate collected or by observing the gel times. The amount of distillate collected depends upon the extent of reaction between acid and amine, and this, in turn, approaches a limit (the gel point) determined by the ratio of difunctional to trifunctional molecules present in the reaction and by the ratio of reactants to one another. Since these factors are known, the extent of reaction at the gel point is readily estimated by the equations of Flory (13). Calculated and observed extents of reaction are expressed herein as per cents of the amount of distillate corresponding to complete reaction of acid (or ester) and amine.

The gel time was determined by placing a small sample of polyamide upon a block heated to 285° C. in air, agitating with a small metal rod such as a nail, and noting the number of elapsed seconds before gelation. This quantity, although approximate, is a very convenient indication of the approach of the gel point, regardless of the degree of reaction at which gelation occurs.

The approximate molecular weight of the polymer was determined by titration of remaining free carboxyl and amino groups and calculation of the respective neutral equivalents. For titration a solution of 10 grams of polymer in 100 ml. of a mixture of equal volumes of *iso*-propyl and *n*-butyl alcohols was used. Carboxyl groups were titrated with 0.1 N. alkali to the end point of phenolphthalein. Amino groups were titrated with 0.1 N. acid, brom-phenol blue being used as indicator.

TABLE II.

Effects of Use of Different Polyamines, and Different Ratios of Amine/Acid, in Polyamide Preparations.

No.	Polymeric fat-acids source	Diamine	Ratio amine/acid (equivalents)	Extent of reaction	Gel time at 285° C.	Molecular weight[1]		Remarks
						Basic	Acidic	
				per cent	*sec.*			
1	Soybean	Ethylene diamine	1.00	95.2	21	7,400	4,100	6 hours additional heating at 200° C. reduced gel time to 18 sec.
2	Soybean	Ethylene diamine	0.80	93.0	32	60,000	1,610	1 hour additional heating at 200° C. reduced gel time to 23 sec.
3	Soybean	Ethylene diamine	1.25	93.0	26	7,800	1,500	Additional heating did not reduce gel time.
4	Soybean[2]	Ethylene diamine	1.02	87.6	33	3,800	3,000[3]	....
5	Soybean	Propylene diamine	1.00	86.0	30	2,070	2,550	Additional heating did not reduce gel time.
6	Soybean	Diethylene triamine	1.00	96.0	10	....	5,270	At incipient gelation.
7	Soybean	Triethylene *tetramine*	1.00	92.0	6	....	....	At incipient gelation.
8	Linseed[2]	Ethylene diamine	1.00	75	19	2,120	....	Gelled after 10 min. at 200° C. at 78 per cent reaction.
9	Linseed[2]	Diethylene triamine	1.00	60.5	28	....	....	Gelled after 15 min. additional heating at 200° C. at 67.4 per cent reaction.
10	Linseed[2]	Triethylene tetramine	1.00	56.0	22	....	....	Gelled after 10 min. additional heating at 200° C. at 60.5 per cent reaction.

[1] Neutral equivalents determined by titration of free amino or corboxyl groups. [2] Polyamides prepared by aminolysis of polymetric fat esters. [3] Obtained by methoxyl determination.

TABLE III.

Effect of Different Dimeric-Trimeric Fat Acid Ratios on Observed and Calculated Extent of Reaction at Gel Point.

No.	Composition of polymeric fat acids		Mole ratio dimer/trimer	Amine	Ratio amine/acid (equivalents)	Calculated extent of reaction for gelation as diamine	Observed extent of reaction without gelation
	Dimer % by wt.	Trimer % by wt.					
						per cent	*per cent*
1	55	45	1.83	Ethylene diamine	1.00	84	95
3	55	45	1.83	Ethylene diamine	0.80	94	93
4	55	45	1.83	Ethylene diamine	1.25	93	93
5	57	43	1.99	Ethylene diamine	1.02	85	87.6
7	55	45	1.83	Diethylene triamine	1.00	84	95
8	55	45	1.83	Triethylene tetramine	1.00	84	92
9	37	63	0.88	Ethylene diamine	1.00	62	78
10	37	63	0.88	Diethylene triamine	1.00	62	67
11	37	63	0.88	Triethylene tetramine	1.00	62	61

When polyamides were prepared from polymeric fat acid esters, the remaining free methoxyl groups were determined by the method of Clark (6).

Discussion of Results

Effect on Gelation of the Ratio of Dibasic to Tribasic Acid. The calculated extent of reaction required for gelation in the condensation of a diamine with a mixture of dibasic and tribasic acids decreases as the ratio of dibasic to tribasic acid decreases. The experimental data (Table III) are in accordance with this expected tendency. The effect of dimer-trimer ratio is also shown by the rate at which the gel time drops upon continued heating (Table II). Thus polyamides from ethylene or propylene diamine and polymeric soybean fat acids do not gel readily, even upon prolonged heating. On the other hand, polyamides from ethylene diamine and polymeric linseed acid esters gel in a relatively short time after attaining a molecular weight of about 2,000.

The observed extents of reaction at gelation were almost uniformly higher than the predicted values, and occasionally they were found to exceed 100 per cent. High results are not without precedent; Flory (13) found that the observed extent of reaction was from 4 to 5 per cent higher than the calculated value for the reaction of ethylene glycol with mixtures of dibasic and tribasic aliphatic acids. Likewise, the results of Kienle and Hovey (14) with glycerol phthalate polymers ranged from 2 to 10 per cent higher than predicted. The occurrence of water as an impurity in the reactants was investigated as one possible cause of extents of reaction in excess of 100 per cent, but it was found not to be the origin of this phenomenon. Another factor that may contribute to the formation of excess water is the occurrence of condensations within the polyamide molecule. However, no entirely satisfactory explanation has been found by the authors.

Effect of Excess Acid or Amine on Gelation. If an excess of acid or amine is used, a decrease in degree of polymerization is obtained, because these conditions operate to reduce opportunity for formation of long polymeric chains (Table II). The theoretical extent of reaction for gelation is 93-94 per cent for amine-acid ratios of 0.8 and 1.25, while that for a ratio of 1.00 is 84 per cent. Observed extents of reaction in these three cases are from 93 to 95 per cent and thus do not distinguish the effect of excess acid or amine. However, at comparable extents of reaction, gel times and molecular weights may be utilized for comparison. The gel times and molecular weights of the polyamides with amine-acid ratios of 0.8 and 1.25 are 32 sec. and 26 sec., and 1,500 and 1,610, respectively, as compared to 21 sec. and 4,100 for the ratio 1.00, showing that the degree of polymerization has been decreased by the use of excess of either reagent.

Effect of Trifunctional and Tetrafunctional Amines on Gelation. In the experiments with diethylene triamine and triethylene tetramine, observed extents of reaction at gelation agree well with those calculated for these amines as difunctional molecules (Table III). Ease of gelation of polyamides of these amines with polymeric fat acids of both low and high dibasic-tribasic acid ratio is in conformity with the expected ease of formation of cross-linkages (Table II). Because the equimolar weights of reactants in these experiments were calculated upon the assumption that polyethylene polyamines would behave as difunctional molecules, an excess of basic amino groups is actually present. This excess is 50 per cent in the case of diethylene triamine and 100 per cent in the case of triethylene tetramine. Gelation at a much

TABLE IV.

Properties of Some Polyamides of Polymeric Fat Acids

Polymeric fat acid source	Diamine	Melting [1] range °C.	Description
1. Soybean	Ethylene diamine	108-112	Hard, brittle non-tacky resin
2. Soybean	Ethylene diamine	104-109	Slightly softer than No. 1
3. Soybean	Ethylene diamine [3]	102-107	Hard brittle non-tacky resin
4. Soybean	Ethylene diamine [4]	92-97	Soft, non-tacky resin
5. Soybean	Diethylene triamine	50-56	Soft, very tacky resin
6. Soybean	Triethylene tetramine	40-45	Soft, very tacky resin
7. Soybean	Propylene diamine	53-59	Medium soft tacky resin
8. Soybean	Hexamethylene diamine	89-93	Hard, brittle non-tacky resin
9. Soybean	Diamine from dimeric fat acids	Not def.	Tough, plastic, somewhat tacky resin
10. Soybean	Hydrazine	101-110	Hard, brittle non-tacky resin
11. Linseed[2]	Ethylene diamine [5]	98-103	Hard, brittle non-tacky resin
12. Linseed[2]	Diethylene triamine	Gelled	Tough, elastic non-tacky resin
13. Linseed[2]	Triethylene tetramine	Gelled	Tough, elastic non-tacky resin

[1] Determined with Parr melting point apparatus. [2] Prepared by aminolysis of the esters. [3] Polymeric acids contained 10 molar per cent monomeric fat acid. [4] Mole ratio amine/acid = 0.8ff1. [5] Mole ratio amine/ester = 1.1:1.

lower extent of reaction would be anticipated if these excesses were not present.

Polyamides from Esters

WHEN polyamides are prepared by aminolysis of polymeric fat acid esters, they are occasionally slightly softer and more tacky, and show somewhat longer gel times than those prepared directly from polymeric fat acids (Table IV). This is particularly true of polyamides of polymeric soybean fat acids where a relatively high degree of reaction (at least 95 per cent) of acid and amine is required to reach the gel point. During the final stage of reaction the concentration of free amino and ester groups has decreased to such an extent that aminolysis of the ester groups becomes very slow. When the polyamide is prepared directly from amine and acid, however, the amine reacts immediately with the acid, possibly forming a "polymeric salt" (12). Dehydration of the salt obviously will proceed by a mechanism which differs from that in the aminolysis reaction, and this dehydration would not be expected to be dependent upon the concentration of free amino or carboxyl groups. After similar periods of reaction a polyamide prepared by aminolysis will therefore represent a lower degree of reaction than one prepared directly from acid and amine. An undue prolongation of aminolysis is required to overcome this difference.

If a lower degree of reaction is required for gelation, e.g., about 78 per cent in the case of ethylene diamine and polymeric linseed fat acids, little difference in physical properties is discernible between polyamides prepared by aminolysis and those prepared by direct reaction of acid and base. In this aminolysis reaction the concentration of amino and ester groups remains relatively high, and the final molecular weight is readily attained.

Copolyamides. Properties of various copolyamides from ethylene diamine and mixtures of polymeric fat acids and sebacic or maleic acid are presented in Table V together with data on the observed and calculated extents of reaction for gelation. The melting points of sebasic acid copolymers were found to bear a linear relationship to the sebasic acid content. Other properties such as hardness and solubility varied in the same way. The extents of reaction achieved in preparing copolymers were again found to be somewhat higher than the calculated values at gelation.

Table V also describes the properties .of several polyamides prepared from polymeric fat acids and mixtures of polyamines. In each case the copolyamide has properties intermediate between those of the polyamides of polymeric fat acids and the separate component polyamines.

Modified Polyamides. Essential data on the preparation and properties of the modified polyamides are given in Table VI. In general, the molecular weights (estimated by determination of acidic and basic neutralization equivalents) were as high as those obtained for unmodified polyamides. The gel times of polyamides modified with monobasic acids were uniformly lower than those of unmodified polyamides from polymeric soybean fat acids, whereas when monofunctional amines were used, the gel times were higher. However, since the gel times did not decrease upon continued heating of the reaction mixture, all modified polyamides were more difficult to gel than the unmodified.

The melting points and dilution ratios of the modified polyamides show substantial variation, and this diversity appears to be due to the presence of the several modifiers rather than to the molecular weight or degree of reaction. These observations are of considerable importance, since solution of problems of melting point, compatibility, gelation, *et cetera,* which arise in the practical utilization of polyamides, may readily be obtained by use of polyamides modified by an appropriate monofunction acid or amine.

Uses for Polyamides

Polyamides from polymeric fat acids have interesting and unusual properties (Table IV) which suggest a variety of applications. For example, they may find new and extended uses in lacquers, adhesives, laminating and heat-sealing agents, plastics, elastomers, paper coatings, ion-exchange resins, and in other outlets.

None of the polyamides, except the ethylene diamine polyamide, has been investigated thoroughly enough to recommend its use at the present time. In preliminary tests it has shown excellent properties in spirit varnishes, lacquers, and paper coatings. It is soluble in relatively inexpensive solvent combina-

TABLE V.

Copolyamides

Acid	Base	Melting range °C.[1]	Calculated extent of reaction for gelation	Observed extent of reaction without gelation	Remarks
			per cent	*per cent*	
1. P. F. A.[2]	Diethylene triamine, hexamethylene diamine (1:1)[3]	80-87			Tough, plastic non-tacky resin
2. P. F. A.	Diethylene triamine, ethylene diamine (1:1)	75-81			Fairly soft, slightly tacky, tough resin
3. P. F. A.	Diethylene triamine, triethylene tetramine (1:1)	43-48			Soft, tacky resin
4. P. F. A., sebacic acid (1:1)	Ethylene diamine	188-196	91	92.7	Insoluble butanol-benzene mixture
5. P. F. A., sebacic acid (2:1)	Ethylene diamine	164-175	88.5	98.0	Insoluble
6. P. F. A., sebacic acid (4:1)	Ethylene diamine	146-155	86.5	97.4	Soluble
7. P. F. A., sebacic acid (8:1)	Ethylene diamine	122-129	85.0	(105)	Soluble
8. P. F. A., maleic acid (4:1)	Ethylene diamine	130-135	86.5	96.0	Soluble

[1] Determined with Parr melting point apparatus. [2] P. F. A. = polymeric (soybean) fat acids. [3] Mole ratios in parentheses.

TABLE VI.

Modified Polyamides.

No.	Monomeric reactant	Extent of reaction	Gel time	Melting range °C.[1]	Acid equiv.	Basic equiv.	Dilution ratio [2]
		per cent	*sec.*				
1	Monomeric fat acid	99.0	31	102-107	2,720	3,475	
2	Stearic acid	96.8	17	115-120	5.580	12,970	19.9
3	Stearic acid [3]	91.8	15	100-104	2,720	3,475	
4	Benzoic acid	96.3	12	100-104	2,490	12,750	15.3
5	Benzoic acid	82.3	15	92-96	2,090	2,740	
6	Abietic acid	(112)	18	100-108	4,370	5,960	16.4
7	Naphthenic acid	(136)	16	94-100	2,500	3,130	13.0
8	*n*-Dodecyl amine	90.0	36	84-90	4,570	6,820	21.6
9	*n*-Dodecyl amine [4]	95.0	36	84-90	4,675	4,450	
10	Monostearoyl ethylene diamine	85.0	36	102-108	4,700	6,650	24.6

[1] Determined with Parr melting point apparatus. [2] Determined by titration of a 30% solution in butanol with Skellysolve C; average value for ethylene diamine polyamide = 13.1. [3] Stearic acid added after ethylene diamine. [4] *n*-Dodecyl amine and ethylene diamine added simultaneously.

tions containing petroleum hydrocarbons and alcohols. It may be applied from a hot melt if properly plasticized or modified. Films of the material show excellent resistance to water, alkali, acid, oils, and grease. Research on the usefulness of this polyamide has been reported (10, 11).

Acknowledgment

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Summary

The preparation and properties of various polyamides, copolyamides, and modified polyamides, of polymeric fat acids have been described. These polymers are of interest because of their unusual properties and because of the unsaturation and relatively high molecular weight of the polybasic acids involved. Despite the presence of tribasic acids in polymeric fat acids, ungelled polymers having molecular weights of 3,000 to 5,000 are obtainable. A brief discussion has been given concerning the application of theoretical principles of polymerization to the preparation of these polymers. Possible industrial uses for the polyamides are indicated.

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Report of the Smalley Foundation Committee 1944-45

WE ARE presenting herewith the 27th report of the Smalley Foundation Committee of the American Oil Chemists' Society. During these past 27 years considerable progress has been made in the accuracy of the determination of oil and nitrogen on cottonseed meal. The results obtained in practically all determinations were slightly higher than last year, with the exception of the oil determinations. It must be understood, in gauging the accuracy of the results, that a difference of two points in either direction from the average is permitted without a deduction from the grade. We might add that the results obtained are so nearly perfect that a few hundredths of a per cent higher or lower than in any previous year means very little as far as accuracy is concerned.

As usual, 30 samples of cottonseed meal were distributed to the collaborators. There are attached to this report four tables indicating the standing in percentage of the members taking part. Table I gives the standing of 45 collaborators who reported oil determinations on all samples. Table II gives the standing of 50 collaborators who reported nitrogen results on all samples. Table III gives the standing of 44 collaborators who reported oil and nitrogen on all samples. In these tables we have taken into consideration the results of those reports which were received within the time specified in our original announcement of the Smalley Foundation work. In Table IV we have given the standing of those collaborators who reported on all samples, but some of whose reports were received too late to be included under the rules. The winning collaborators are as follows:

The American Oil Chemists' Society Cup for the highest efficiency in the determination of both oil and nitrogen on all samples is awarded to Analyst No. 53, W. W. Wynn, Jr., Barrow-Agee Laboratories, Cairo, Illinois, with an average of 99.957%. The average efficiency is higher than that of last year, which was 99.953%. The certificate for second place goes to Analyst No. 55, D. B. McIsaac, Kershaw Oil Mill, Kershaw, S. C., who had an efficiency of 99.950%, as compared with 99.947% for last year.

The certificate for the highest efficiency in the determination of oil only is awarded to Analyst No. 55, D. B. McIsaac, Kershaw Oil Mill, Kershaw, S. C., with an average of 99.973%, as compared with 99.980% for last year. The certificate for second place goes to analyst No. 53, W. W. Wynn, Jr., Barrow-Agee Laboratories, Cairo, Illinois, with an efficiency of 99.937% as compared with 99.948% for last year.