Polymerization of Unsaturated Fatty Acids[*]

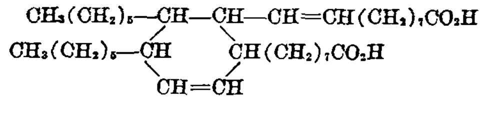
CHARLES G. GOEBEL
Emery Industries, Inc., Cincinnati, Ohio

Introduction

THE purpose of this paper is to describe a novel method for the preparation of polybasic fat acids by the direct polymerization of unsaturated fatty acids by heat without a resulting appreciable loss in carboxy acidity. In this process decarboxylation and decomposition which heretofore invariably have accompanied heat polymerizations of fatty acids are prevented by the presence of moisture maintained in the reaction vessel by steam pressure. Besides its stabilizing effect on the carboxyl group, the moisture which is present also changes the composition of the polybasic fat acids in that the ratio of dibasic fat acids to higher polybasic fat acids is shifted considerably in favor of the dibasic acids as shown by polyamide preparations and molecular distillations. This process of polymerization in the presence of moisture has also been used to remove polyunsaturated acids from commercial oleic acid.

The results have been sufficiently promising to warrant the preparation of patent applications which are now pending with the expectation that the processes will find commercial utilization in the near future.

The subject of oil polymerization and the mechanism by which it takes place has been the basis for numerous investigations not only because of the widespread practical use of the process but also in order that a satisfactory working theory might be provided. Most of the early work on this general subject dealt with the mechanism of oil polymerizations. Schreiber (1), who was one of the early workers in the field, advanced the theory that the isomerization of nonconjugated systems is a prerequisite to the polymerization reaction. Kappelmeier (2) suggested that the polymerization took place by a diene reaction or 1,4 addition of an isomerized molecule to a double bond of another molecule to form a substituted cyclohexene derivative. These theories were supported by Bradley and coworkers (3, 4) who investigated the course of polymerization of drying and semi-drying oils and determined the constitution of drying oil gels. During the course of the latter work, these investigators (5) isolated and characterized a fraction of polybasic acids which they termed "dimer" acids. According to the postulated mechanisms, the structural formula for dimerized linoleic acid would be,



More recent work by Bradley and Johnston (3, 4) has shown that trimeric esters as well as dimeric esters are formed when methyl linoleate obtained from dehydroxylated castor oil is polymerized by heating. Cowan and coworkers (6) have shown by molecular distillations of materials obtained by the polymerization of methyl esters of linseed fatty acids that more than 50% of the polymerized esters are trimeric and higher polymeric in nature. When the polymerized esters are split, polybasic fat acids are formed. Polyamides of these materials have been suggested as adhesives and shellac substitutes, and the polyglycol esters of the polybasic fat acids were tested as rubber substitutes during the war. The proposed uses have encouraged various investigators to introduce methods for the preparation of these polybasic fat acids as such.

There are four principal methods for the preparation of polybasic fat acids. Unsaturated glycerides are polymerized by heat in an inert atmosphere until the gel point is nearly reached. This material is then split by alkali, and the acids are recovered by acidification of the soaps. Unpolymerized acids are removed by distillation under reduced pressure. In this process the yield of polybasic fat acids seems to be limited by the gel point of the oil used. The second process utilizes a methanalysis reaction of a drying oil and methanol in the preparation of the methyl esters of the unsaturated fat acids. The methyl esters are then polymerized by heat, after which the material is distilled under reduced pressure to remove the unreacted portion. The residual esters are then split with alcoholic caustic solution, and the free acids are obtained by acidification of the soaps. These two methods are described in detail by Cowan (7, 8) and Bradley (9). Percy and Ross (10) have described a method of preparing polybasic fat acids by the heat polymerization of the anhydrous sodium soaps of unsaturated fatty acids. The free acids are obtained by the acidulation of the soaps and are separated by distillation. Polybasic fat acids have been prepared by the heat polymerization of the fatty acids directly, with the separation being made by distillation. This would seem to be the most economical and direct method of preparing polybasic fat acids, but all of the reports on this procedure point out the fact that the fatty acids tend to decompose and decarboxylate when heated at or above 275°C., which is lower than the usual polymerization temperature of 300°C. In fact, it has been found in our laboratories that when linseed fatty acids are polymerized at 280 to 290°C., in an inert atmosphere, polybasic fat acids are obtained which constitute 50 to 55% of the weight of the starting acids but which have lost 30 to 35% of the original acidity by decarboxylation. Since it is desirable to prepare polybasic fat acids directly from fatty acids without appreciable loss in carboxy acidity, the following procedure, which is the basis of this paper, was developed.

Experimental

The fatty acids used in the experimental work were commercial grade fatty acids. Heat polymerizations of the unsaturated fatty acids in the presence of moisture were carried out in a stainless steel pressure vessel which was heated by a direct gas flame.

Polybasic Fat Acids: A sample of the unsaturated fatty acids was put into the pressure vessel along with a small amount of water and heated to 330 to 360°C. The pressure was adjusted to the desired value of 85 to 400 lbs./in.^{2} by the use of a vent valve. As an

---

[*] Presented at 20th fall meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 30-Nov. 1, 1946.

alternate method, the pressure vessed was connected directly to a steam line. After the heating period of 3 to 8 hours the partially polymerized acids were dried, and the unreacted portion was removed by distillation under reduced pressure. The color of the polybasic acids in some runs was improved by bleaching with 3% of bleaching earth for 40 minutes at 80 to 90°C. The products were characterized by iodine values and neutralization equivalents. Results of typical polymerizations are tabulated:

Raw Material	I.V.	N.E.	Polybasic Fat Acids			Monobasic Acids		
			%	I.V.	N.E.	%	I.V.	N.E.
Linseed Acids	190	286	63.3	102.5	303	36.7	85	277
Cottonseed Acids	135	293	50.5	88	315	49.5	80	292
Soy Acids	136	282	58.5	81	311	41.5	60	280

Polyamides From Polybasic Fat Acids: Polybasic fat acids were used to prepare polyamides with both ethylene diamine and hexamethylene diamine. Polybasic fat acids were heated with stirring to 150°C. and with a slow stream of carbon dioxide gas being passed through them. A chemical equivalent of ethylene diamine (70% aqueous solution) was added slowly through a tube leading to the bottom of the reaction vessel. When all of the ethylene diamine had been added, the temperature was raised gradually to 200°C., and the pressure was lowered to 10 mm. of Hg. After one hour at these conditions a sample was removed and titrated with both acid and base to determine which ingredient was in excess. A calculated amount of the lesser ingredient was added, and the temperature was raised to 250 to 260°C. under 10 mm. of Hg. pressure. Polyamides having molecular weights of 6,000 to 10,000 were obtained in this manner.

Chemical equivalents of polybasic fat acids and hexamethylene diamine were heated in the presence of carbon dioxide gas at 150°C. for one hour. The temperature was then raised to 200°C., and the pressure was reduced to 10 mm. of Hg. After one hour, a sample was removed and titrated with acid and base to determine the ratio of free carboxyl to free amino groups. Any inequalities were adjusted, and the resin was heated to 250 to 260°C. under a pressure of 10 mm. of Hg. Polyamides having molecular weights of 28,000 to 29,000 were obtained by this method.

Molecular Distillations: The methyl esters of polybasic fat acids from various raw materials were prepared. They had free fatty acid values of about 2% as oleic acid. The esters were heated to 300°C. under 4 mm. of Hg. pressure to remove gases and any unremoved monomeric esters. Samples were weighed into a Hickman molecular still and were distilled at temperatures up to 250°C. under a pressure of one to two microns. The distilled esters were mobile liquids having free fatty acid values in the order of 0.2% as oleic acid.

Removal of Polyunsaturated Acids From Commercial Oleic Acid: Only slight variations in the polymerization process need be made for removing polyunsaturated acids from commercial oleic acid. Usually a shorter time and a lower temperature are used.

Commercial oleic acid was heated in an autoclave for three hours at 330 to 340°C. under a steam pressure of 300 lbs./in.^{2}. Monomer acids were removed from the polymerized acids by distillation under reduced pressure. Spectrophotometric results showed that the polyunsaturated acid content had been substantially lowered. Results of a typical run are tabulated.

Material	%	I.V.	N.E.	Polyunsaturated Acid Content %
Commercial Oleic Acid	100	95	286	11.9
Distillate	85	83	283	2.7
Residue	15	80	556	......

Discussion

The process for the preparation of polybasic fat acids directly from the acids is a very simple one involving two steps which are polymerization and separation. It is based on the discovery that small amounts of water maintained in the reaction vessel almost completely stop decomposition of the fatty acids at polymerization temperatures. The use of moisture in conjunction with heat and moderate pressures is a very simple process to apply commercially, and perhaps because of its simplicity is surprisingly effective. The various factors effecting this process are the nature of the raw material used, polymerizing temperatures, time of polymerization, moisture present, and catalysts.

Raw materials: Fatty acids from any of the many drying or semi-drying oils may be used, but from the standpoint of economics, fatty acids recommended are those from soy, cottonseed, corn, and linseed oils. In this process the yield of polybasic fat acids obtained seems to be limited by the amount of polyunsaturated acids present in the raw material used (Table I). In general, the color and quality of polybasic fat acids are dependent on the color and quality of the raw material. The amount of polyunsaturated fatty acids having more than two double bonds to a molecule is a factor in determining the amount of tribasic and higher polybasic fat acids formed during the polymerization. This is demonstrated by the fact that linseed fatty acids, which contain considerable linolenic acid, produce more tribasic acids than do fatty acids from soy oil which have much lower linolenic acid content.

TABLE I

Effect of Raw Material on Yield of Polybasic Fat Acids Obtained

Raw Material	I.V.	Yield of Polybasic Acids
Soy Acids	137	58.5
Linseed Acids	190	64.2
Linseed Acids	208	76.8
Cottonseed Acids	134	50.5
Cottonseed Foots Acids	109	39.5

Time and Temperature of Polymerization: The polymerizing temperatures used were from 275 to 370°C. The temperature at which the reaction is carried out does not seem to be critical, but there is an interrelationship between time and temperature in that higher temperatures shorten the time of polymerization appreciably. For example, about the same degree of polymerization is attained in six to seven hours at 350°C., as results from an 18-hour heating period at 290°C. In order to obtain a high degree of polymerization in a reasonable length of time, temperatures of 330 to 360°C. are recommended. At these temperatures, polymerization is virtually complete in three to eight hours.

Presence of Moisture: The presence of moisture in the polymerization reaction produces remarkable results, but the exact function of the moisture from a theoretical standpoint has not been satisfactorily explained. It may be that it is a question of decomposition pressures in which the water vapor prevents the splitting out of water from the fatty acids, or it may be that the loss of carboxy acidity is prevented by water dissolved in the fatty acids during the reaction at high temperatures. It is known, however, that the moisture does not act in the manner as does an inert atmosphere such as nitrogen or carbon dioxide gas, or as a simple diluent such as petroleum hydrocarbon (Table II). The moisture which usually amounts to 1 to 5% of the weight of the fatty acids is kept in the reaction vessel by means of pressure. Steam pressures below 80 lbs./in.^{2} allow slow decomposition of the fatty acids; whereas steam pressures of 85 to 400 lbs./in.^{2} substantially prevent loss of carboxy acidity. Although much higher steam pressures may be used ranging up to the steam pressures of saturated steam at the temperatures involved, pressures above 400 lbs./in.^{2} are unnecessary and only add to the cost of the equipment which must be used.

TABLE II

Decomposition in Presence of CO_2 as Compared to H_2O

Time (Hrs.) at 350°C.	N.E. 200 lbs./in.^{2} CO_2	N.E. 200 lbs./in.^{2} steam
0	286	286
0.5	295	288
1.0	315	288.5
2.25	458	291
3.0	517	292
4.5	798	293

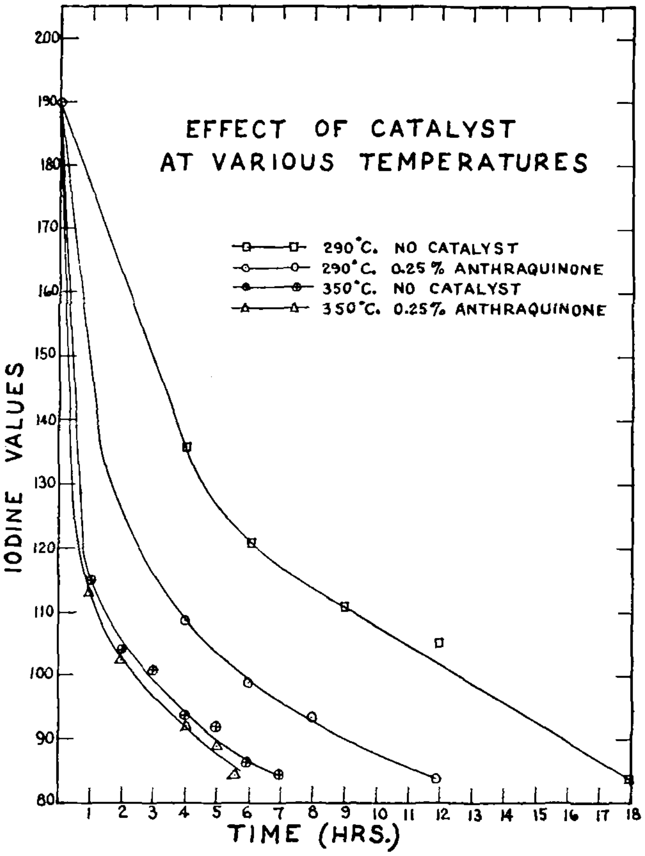


FIG. 1

Catalysts: Various catalysts may be employed to accelerate the polymerization reaction and to improve the yields of polybasic fat acids; however, at higher temperatures, the acceleration due to catalysts being present is lessened, and the improvement in yields is very small (Fig. 1). Since the polymerization at temperatures of 330 to 360°C. takes place quite rapidly without catalysts, and an additional step is required for their removal, their importance in this process is only slight. A partial list of catalysts tried includes mercuric acetate, lead acetate, anthraquinone, and Raney nickel, with mercuric acetate and Raney nickel giving the best results.

Nature of Products: The polybasic fat acids obtained by this process are fundamentally the same type of materials as those obtained from any of the previously described processes, but the components are in a much different ratio. The difference in composition was first noticed when polyamide resins were prepared by heating the polybasic fat acids with ethylene diamine in a manner similar to that described by Cowan and coworkers (11). Polyamides prepared from chemically equivalent quantities of ethylene diamine and polybasic fat acids of the conventional methods showed a marked tendency to gel in from 20 minutes to 2 hours at 200°C. under a pressure of 10 mm. of Hg., depending on whether linseed or soy esters were used as the raw material. Samples of polyamides prepared from ethylene diamine and polybasic fat acids from linseed acids by the direct method were heated at 250 to 260°C. for 20 hours under 10 mm. of Hg. pressure before signs of gelation appeared; whereas, when polybasic acids from soy or cottonseed acids were used, the polyamides showed no signs of gelation even after 48 hours of heating at 250 to 260°C. Using hexamethylene diamine and polybasic fat acids from cottonseed acids, polyamides have been prepared having molecular weights of 28,000 to 29,000 without gelation occurring. To verify this difference in composition of the polybasic fat acids of this process and the conventional methods, the methyl esters of the acids were prepared and subjected to molecular distillations (Table III).

TABLE III

Comparison of Molar Dibasic to Tribasic Acid Ratios in Polybasic Acids

Raw Material	Process	% Dimer	% Trimer	Molar Ratio—Dimer/Trimer
Soy Acids	Direct	91.9	8.1	17/1
Cottonseed Acids	Direct	90.0	10.0	13.5/1
Linseed Acids	Direct	83.5	16.5	7.5/1
Soy Esters	Conventional	63.7	36.3	2.6/1

Cowan and coworkers (6) have reported that when linseed esters were polymerized, the dibasic acid content was approximately 35% and the tribasic and higher polybasic acid content was about 65%. This gives a molar dimer/trimer ratio of 0.81/1. When esters of soybean fatty acids were polymerized by their method, the dibasic acid content was about 57% and the tribasic and higher polybasic acid content was about 43%. This gives a molar dimer/trimer ratio of 1.98/1. Other ratios of dimer/trimer on products from their process varied from 1.5/1 to 3.4/1, depending on whether linseed or soy esters were used for the polymerization reaction. In uses where gelation is to be avoided, a material having a lower tribasic acid content would offer a distinct advantage.

The color of the polybasic fat acids, as mentioned earlier, varies with the color and quality of the fatty acids used. During the polymerization reaction some darkening occurs but, on drying and bleaching the material with 2 to 5% of bleaching earth, the original color of the acids can be restored. When the acids are separated by removing the monobasic acids by distillation, the color change in the polybasic fat acids is very little more than would be expected due to color concentration by removing the practically colorless distillate. Colors of the polybasic acids range from yellow to amber.

Yields: The yield of polybasic fat acids, as has been previously stated, depends on the raw material used. This is due to the fact that practically all of the polybasic fat acids produced are derived from the polyunsaturated acids present in the raw material. Nearly all of the polyunsaturated acids are polymerized during a six- to eight-hour heating period at 340 to 350°C., and the yield of polybasic fat acids agrees very closely with the amount of polyunsaturated acids removed from the raw material (Table IV). The factors of time and temperature also determine the yield obtained from any given raw material in that a longer time is required at lower temperatures to give a corresponding yield. At 350°C., however, heating periods of longer than six to eight hours fail to improve yields substantially (Table V).

TABLE IV

Comparison of Yields of Polybasic Acids and Polyunsaturated Acids Removed From Starting Acids. Runs Made for Seven Hours at 350°C.

Raw Material	% Polyunsaturated Acids in Raw Material	% Yield of Polybasic Acids	% Polyunsaturated Acids Unreacted
Linseed Acids	63.3	62.3	0.71
Cottonseed Acids	50.4	50.5	0.89

TABLE V

Variation of Yields With Time of Reaction at a Given Temperature

Raw Material	Time (Hrs.)	Temperature (°C.)	Yield (%)
Cottonseed Acids	8	350	43
Cottonseed Acids	7	350	49
Cottonseed Acids	22	350	50.5
Linseed Acids	3	350	56
Linseed Acids	7	350	63.5

Other Uses of Process: This method of direct polymerization of fatty acids in the presence of moisture has been used successfully for removing the polyunsaturated fatty acids from commercial oleic acid which usually contains 8 to 15% of fatty acids having more than one double bond per molecule. Samples of oleic acid containing less than 3% polyunsaturated acids have been prepared by heating commercial oleic acid at 340 to 350°C. for 2.5 to 3 hours, after which separation of the products was effected by distillation under reduced pressures. A comparison of the oleic acid produced with the raw material used is given in Table VI. A still residue of 10 to 15% of polymerized acids is obtained depending on the polyunsaturated acid content of the commercial oleic acid used. The color of the distilled material is very good. Colors of 1 to 2 yellow by 0 to 0.2 red on a 5¼" column of a Lovibond scale are readily obtained. The oxygen stability of the treated oleic acid is also substantially improved as shown by Mackay tests.

TABLE VI

Comparison of Commercial Oleic Acid With That From Which the Polyunsaturated Acids Have Been Substantially Removed

Type of Oleic Acid	I.V.	FFA as Oleic	Total Polyunsat.	Unsap.	Titre °C.
Commercial Oleic Acid	95	98.5	11.9	1.3	2.3
Treated Oleic Acid	83	99.5	2.8	1.2	9.4

Summary

A method is proposed for the preparation of polybasic fat acids or "dimer" acids directly from fatty acids which is readily adaptable to commercial use. The presence of moisture maintained in the reaction vessel by steam pressure substantially prevents decomposition and decarboxylation of the fatty acids. By this method a larger percentage of dibasic acids, as compared to tribasic acids, is produced than by the previously described methods. The method of high temperature polymerization of fatty acids in the presence of moisture is also used to remove polyunsaturated fatty acids from commercial oleic acid.

Acknowledgment

The author wishes to express his appreciation to W. C. Clark who made the spectrophotometric determinations recorded in this paper.

REFERENCES

1. Schreiber, J., Farbe u. Lack, *1929*, 585-7.
2. Kappelmeir, C. P. A., Farben-Ztg., *38*, 1018, 1077 (1933).
3. Bradley, T. F., and Johnston, W. B., Ind. Eng. Chem., *32*, 802 (1940).
4. Bradley, T. F., and Johnston, W. B., *Ibid.*, *33*, (1941).
5. Bradley, T. F., and Pfann, H. F., *Ibid.*, *32*, 694 (1940).
6. Bulletin NM-248A, Progress Report: *Norepol And Its Derivatives*, U. S. Dept. of Agriculture, August 23, 1943.
7. Cowan, J. C., and Ault, W. C., U. S. Patent 2,373,015 (1945).
8. Cowan, J. C., and Teeter, H. M., U. S. Patent 2,384,443 (1945).
9. Bradley, T. F., U. S. Patent 2,379,413 (1945).
10. Percy, J. H., and Ross, J., U. S. Patent 2,341,239 (1944).
11. Falkenburg, L. B., Teeter, H. M., Skell, P. S., and Cowan, J. C., Oil and Soap *22*, 143 (1945).