Table VII. Decomposition of Citrus Leaf Powder on Storage

Storage Period, Months	Loss in Nitrogen, % Sealed bottle on shelf	Sealed bottle in refrigerator at −5° C.
1	0	0
2	1.2	0
3	3.6	0.2
4	7.0	0.1
5	10.0	0.2

must be carefully studied and a satisfactory treatment program must be worked out. As a result of this study, the following procedure is recommended for the preparation of citrus and pineapple leaves.

Procedure for Citrus Leaves. After picking, the leaf samples should be transported to the laboratory as quickly as possible, transferred to polyethylene bags, and stored in a refrigerator. One sample is removed at a time from the refrigerator, and each individual leaf is washed by first thoroughly sponging both sides with cotton wool in a 0.1% Teepol solution, and then rinsing well with different amounts of pure water. When the whole sample is washed, the water is drained off, and the midribs of the leaves are cut out with stainless steel scissors, to facilitate grinding and drying, as well as to give a more representative sample of the lamina. The leaf halves are then placed in a clean muslin bag and suspended inside a forced-draft oven, set at 65° C. After drying for 48 hours at this temperature, the sample is ground in an all-agate mechanical ball mill. After grinding, to remove the moisture picked up during this step, the leaf powder is placed in a clean bottle and dried for a further 24 hours at 65° C. A subsample may then be weighed out for chemical analysis, or the bottle may be sealed and stored under refrigerated conditions until such time as the analysis can be carried out.

Procedure for Pineapple Leaves. Pineapple leaves are washed as described above. After washing, the middle third of the white, meristematic basal tissue is cut out (*16*) and placed in a clean muslin bag. The sample is dried as above, but at 50° C., and the drying is carried on for 72 hours. The grinding and final drying of the leaf powder are exactly the same as for citrus leaves.

Acknowledgment

The author is indebted to the South African Council for Scientific and Industrial Research for generous financial assistance.

Literature Cited

(1) Bathurst, A. C., D.Sc. thesis, University of Stellenbosch, S. Africa, 1948.
(2) Boynton, D., Burrell, A. B., *Proc. Am. Soc. Hort. Sci.* **44,** 25 (1944).
(3) Chapman, H. D., Brown, S. M. *Hilgardia* **19,** 501 (1950).
(4) Cooper, M. D., *Anal. Chem.* **25,** 411 (1953).
(5) Fortune, W. B., Mellon, M. G. *Ind. Eng. Chem., Anal. Ed.* **10,** 60 (1938).
(6) Goodall, D. W., *J. Pomol. Hort. Sci.* **20,** 136 (1943).
(7) Hood, S. L., Parks, R. Q., Hurwitz, C., *Ind. Eng. Chem., Anal. Ed.* **16,** 202 (1944).
(8) Jacobson, L., *Plant Physiol.* **20,** 233 (1945).
(9) Lundblad, K., Svanberg, O., Ekman, P., *Plant and Soil* **1,** 277 (1949).
(10) McKenzie, H. A., Wallace, H. S., *Australian J. Chem.* **7,** 55 (1954).
(11) Mann, C. E. T., Wallace, T., *J. Pomol. Hort. Sci.* **4,** 146 (1925).
(12) Nicholas, D. J. D., Lloyd-Jones, C. P., Fisher, D. J., *Nature* **177,** 336 (1956).
(13) Piper, C. S., "Soil and Plant Analysis," p. 253, Hassell Press, Adelaide, Australia, 1942.
(14) Sideris, C. P., Krauss, B. H., Young, H. Y., *Plant Physiol.* **13,** 489 (1938).
(15) Steyn, W. J. A., *J. African Chem. Inst.* **9,** 39 (1956).
(16) Steyn, W. J. A., Ph.D. thesis, Rhodes University, Grahamstown, S. Africa, 1957.
(17) Tauber, H., "Chemistry and Technology of Enzymes," p. 4, Wiley, New York, 1949.
(18) Thomas, W., *Soil Sci.* **59,** 353 (1945).
(19) Ulrich, A., in "Diagnostic Techniques for Soils and Crops," p. 157, Am. Potash Inst., Washington, D. C., 1948.
(20) Verdier, E. T., Steyn, W. J. A., Eve, D. J., J. AGR. FOOD CHEM. **5,** 354 (1957).
(21) Willits, C. O., *Anal. Chem.* **23,** 1058 (1951).
(22) Yuen, S. H., Pollard, A. G., *J. Sci. Food Agr.* **6,** 223 (1955).

Received for review November 11, 1958. Accepted February 19, 1959.

FOOD ADDITIVE EVALUATION

Cloud Point as a Means of Characterizing the Polyglycols of Polyoxyethylene (8) Stearate

M. D. BREWSTER and J. D. BRANDNER

Atlas Powder Co., Wilmington, Del.

Polyoxyethylene (8) stearate which has been used extensively in yeast-raised baked goods may be characterized by the cloud point of the recovered polyethylene glycols. This test is sensitive to the molecular weight distribution of the polyglycols in the mixture and hence will distinguish between polyethylene glycols which have a Poisson-type distribution and those of the same average molecular weight but having a nonrandom distribution of polyethylene glycols. Cloud point is particularly sensitive to the presence of polyethylene glycols of molecular weight greater than 600.

POLYOXYETHYLENE (8) STEARATE (Atlas Powder Co., MYRJ 45) is made by reaction of ethylene oxide with commercial stearic acid. MYRJ 45 has been used extensively in yeast-raised baked goods, where it acts as a dough conditioner and retards firming. This product contains monoesters, diesters, and unesterified polyglycols. Esterified and free polyol portions of polyoxyethylene (8) stearate are essentially identical (*1*), and are mixtures of various molecular weight polyglycols having a Poisson distribution, as predicted by Flory (*2*), and average molecular weights between 335 and 350. To characterize MYRJ 45, it is desirable to distinguish between its polyol mixture and poly(ethylene glycol) mixtures having substantially different distributions of poly(oxyethylene glycols). Hydroxyl number and other determinations such as oxyethylene content (*3*) will distinguish between mixtures differing in average molecular weight, but to distinguish between mixtures which by chance or design have the same average molecular weight but a radically different distribution of polyglycols, an additional test, sensitive to poly(ethylene glycol) distribution was sought.

In attempts to obtain such a test, such characteristics as freezing point,

Table I. Description of Materials

Source	Sample	Hydroxyl No.	Calcd. Av. Mol. Wt.
Total polyols from polyoxyethylene (8) stearate	A	321	350
	B	332	338
Free polyols from polyoxyethylene (8) stearate	C	333	337
	D	323	348
	E	331	340
Commercial diethyleneglycol	F	1023	110
Commercial polyglycol			
200	G	554	203
400	H	290	387
600	J	182	618
1000	K	113	993
Blend of			
76.7% K, 23.3% F	L	330	340
51.8% K, 48.2% G	M	324	347
61.2% J, 38.8% G	N	328	343

Table II. Cloud Points of Various Poly(ethylene Glycol) Mixtures

Sample	Av. Mol. Wt.	Cloud Point, °F.
A	350	28
B	338	22
C	337	22
D	348	24
E	340	26
Av.	343	24 ± 3
H	387	36
J	618	74
K	993	115

Table III. Cloud Points of Poly(ethylene Glycol) Mixtures of Equal Average Molecular Weight

Sample	Av. Mol. Wt.	Cloud Point, °F.
A–E, av.	343	24
L	340	96
M	347	90
N	343	58

viscosity, and refractive index of a number of polyethylene glycol mixtures were determined. Only cloud point determinations were sufficiently affected by polyglycol distribution to be useful as a means of distinguishing between the polyglycol mixture occurring in polyoxyethylene (8) stearate and mixtures which contained appreciably higher molecular weight polyethylene glycols.

Experimental

Materials The total polyglycols from polyoxyethylene (8) stearate used in this investigation (Table I) were obtained by saponification of MYRJ 45 and the free or unesterified polyols were obtained from MYRJ 45 by a solvent extraction procedure (*1*). Tests also were made on some commercially available polyglycols and mixtures thereof.

Procedure. Cloud points of the polyethylene glycol mixtures were determined by ASTM Method D 97-47. Essentially this consists of cooling a sample under specified conditions and determining the temperature at which a ring of haze is first observed at the bottom of the container. The specified accuracy of this test is to ±5° F.

Average molecular weights reported herein were calculated from hydroxyl number determinations by a modification of the method of West, Hoagland, and Curtis (*4*). The accuracy of this determination is to better than ±2%.

Table IV. Cloud Points of Mixtures of Polyoxyethylene (8) Stearate Polyols and Other Polyglycols

Composition of Mixture, %		Cloud Point, ° F., of Mixture Containing MYRJ 45 Polyol and Indicated Glycol					
MYRJ 45 polyol	Glycol added	H	J	K	L	M	N
100	0	24[a]	24[a]	24[a]	24[a]	24[a]	24[a]
98	2	..	24	62	62	57[a]	26
95	5	..	34	74	72	71[a]	20
90	10	28	38	78	80	72	30
70	30	..	..	..	..	84	44
0	100	36	74	115	96	90	58

[a] Average of determination on mixtures with A through E; other with A only.

Table V. Effect of Water on the Cloud Point of Polyoxyethylene (8) Polyols

Water, %	Cloud Point °F.
0.2[a]	24
2.0	22
5.0	12
10.0	0
15.0	−13
20.0	−34

[a] Data of Tables I through IV are based on samples having water contents in range 0.1 to 0.5%.

Results and Discussion

The cloud points of the above poly(ethylene glycols) were determined (Table II).

The cloud point of poly(ethylene glycol) mixtures increased as the average molecular weight of the mixture increased, and the total and free polyols of various batches of polyoxyethylene (8) stearate had comparable and uniform cloud points.

The effect on cloud point of the distribution of various molecular weight poly(ethylene glycols) in mixtures of the same average molecular weight was then investigated. Samples of the commercial polyglycols were blended in proportions such that the average molecular weights of the mixtures were comparable to that of the polyols from polyoxyethylene (8) stearate. Cloud points of these mixtures are shown in Table III.

These results indicated that poly(ethylene glycol) mixtures of the same average molecular weight, but differing in polyglycol distribution do not have equal cloud points. The cloud point of the mixture appeared to increase as the difference between the molecular weight of the components and the average molecular weight of the mixture increased. For example, sample L, obtained by combining polyols having average molecular weights of 110 and 993, had a cloud point of 96° F., while sample N, made by blending polyols having average molecular weights of 203 and 618, had a cloud point of 58° F.

Cloud point data also were obtained on other mixtures prepared by combining the above polyglycols with polyols from polyoxyethylene (8) stearate (Table IV).

These data showed that the cloud point of poly(ethylene glycol) of average molecular weight 340 was sensitive to the presence of 5% of poly(ethylene glycol) of average molecular weight 600, and to as little as 1% of poly(ethylene glycol) of average molecular weight 1000.

The effects of such impurities as ash, ester, and water in the polyols from polyoxyethylene (8) stearate on cloud point were determined. Less than 0.5% of stearate ester, sodium stearate, or sodium sulfate was soluble in this poly(ethylene glycol) mixture, and this amount has no observable effect on the cloud point of the mixture. Water in amounts up to 20% lowered the cloud point of these mixtures by about 3° F. for each per cent of water present (Table V).

Literature Cited

(1) Birkmeier, R. L., Brandner, J. D., J. Agr. Food Chem. **6,** 471–5 (1958).
(2) Flory, P. J., *J. Am. Chem. Soc.* **62,** 1561–5 (1940).
(3) Morgan, P. W., *Ind. Eng. Chem., Anal. Ed.* **18,** 500 (1946).
(4) West, E. S., Hoagland, C. L., Curtis, G. H., *J. Biol. Chem.* **104,** 627 (1934).

Received for review December 12, 1958. Accepted February 26, 1959.