

Fig. 4. Theoretical whiteness retention.

One point of view which is highlighted by this material is that the effects of the addition of builders to detergent solutions may be primarily the alteration of the soil and fabric rather than changes in the properties of the solution itself.

We realize, of course, that the removal of dirt and the prevention of its deposition need not be identical processes. On the other hand, there are indications that they are closely related. Detergent solutions will not, in general, remove solid dirt from a surface just by soaking. Some mechanical action is necessary. It appears that the decomposition of the fabric-dirt complex can be considered to be a process promoted by mechanical action. In plain water mechanical action may merely shift the dirt from one site to another on a fiber or transfer it from fiber to fiber. Whereas in the presence of detergent this transfer does not take

While whiteness retention experiments have interest in connection with detergency evaluations, we were especially concerned with, first, the demonstration of the stoichiometry of the reaction between dirt and soap and second, the relevance of the zerointercept, in the graph of critical soap concentration against amount of dirt, to the function of micelles in detergency.

REFERENCES

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Report of the Glycerin Analysis Committee 1947-1948

URING the two years since the last formal report (1) to the Society, the Glycerin Analysis Committee has applied the recently revised methods of analysis to six cooperative samples representing the types of material most often encountered in the production of commercial glycerin. These samples were: a) salt and glycerin lye from kettle soap boiling; b) salt crude glycerin made by the evaporation and concentration of S. & G. lye; c) commercial C. P. distilled glycerin; d) salt plus added glycerin in water solution to simulate the salt recovered in the evaporation of S. & G. lye; e) saponification crude glycerin; and f) saponification sweetwater from which saponification crude is made by evaporation and concentration. The last two samples result from the hydrolysis of fatty oils by various processes for the manufacture of fatty acids.

Periodic Acid Method

The periodic acid method of analysis was applied to all samples. The usefulness of this method has

been demonstrated in our last report where it was shown to be unaffected by the usual impurities found in commercial and process samples. However its standard deviation, on 100% glycerin basis, for the two crudes, the S. & G. lye, and the saponification sweetwater is about 1% in comparison with about 0.5% for the C. P. distilled glycerin. Several suggestions for the improvement of this method will receive consideration during the coming months. Meanwhile the committee recommends that the "tentative" status of the method be continued with the following rewritten version of one section:

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F. Note:

3. The glycerol content of the sample tested must be between 0.1200 and 0.1500 gram for samples containing more than 10% glycerol except in cases like sweetwater concentrate where the excess of periodic acid given below is used to indicate when the proper

A.O.C.S.	GLYCERIN	ANALYSIS	COMMITTEE	1947-1948
	Sample "A	"_Salt and	Glycorin Lyo	

Member	1	2	3	5	6	7	8	9	10	Average	Standard Deviation	Number of Analyses
Laboratory Analysis												
% Glycerin Periodic Acid Method	9.32	9,56	9.45	9.3	9.33	9.24	9.3	9.39	9.34	9.36	0.09	9
Gross Acetin			8.92	••••	,							1
Dichromate	•••••	*****		••••	9.27	9.24	9.3	2.22		9.27	0.02	3
Permanganate		• • • • • • • • • • • • • • • • • • • •			•••••		• • • • •	9.73				1
% NaCl	11.60	12.20	12.03	12.1	12,08	11,95	11.9	12.79	12.12	12.09	0.30	9

Sample	"F"-	-Saponification	Sweetwater

Laboratory Analysis									i			İ
% Glycerin by Periodic Acid	11.53	11.56	11.73	11.58	11.58	11.44	11.60	11.24	11.55	11.53	0.13	9
% Glycerin Gross Acetin	*****	*****	11.50	*****		*****	*****	******				11

A.O.C.S. GLYCERIN ANALYSIS COMMITTEE 1947-1948
Sample "B"—Salt Crude Glycerin

Member	1	2		8	3		-	5	6		7
Member	A	A	A	В	C	D	A	В	A	A	В
Laboratory Analysis		i — i					1				
% Ash	8.99	8.84	9.18	9.05	9.02	9.30	9.11	9.2	9.11	9.20	8.52
% Total Alkalinity as Na ₂ O	0.80	0.72	0.79			******	0.77	0.78	0.80	0.82	0.86
% Free Caustic Alkalinity, as Na ₂ O,	0.005	0.012	0.02	•••••			0.01	0.02	0.02	0.01	0.025
% Carbonate Alkalinity as Na ₂ O	0.035	0.046	0.02	******	******	*******	0.08	0.02	0.06	0.06	0.055
% NaCl	6.90	6.97	7.02	7.12	6.99	7.36	7.12	7.13	7.17	6.95	6.83
% Alkalinity Comb. with or Equiv. to Organic Acids	0.76	0.67	0.75			•••••	0.68	0.74	0.73	0.75	0.78
% Total Residue at 160°C	10,48	9.52	10.86	10.86		11.08	10.98	11.04	11.08	11.64	10.63
% Organic Residue at 160°C	1.49	0.68	1.68	1.81	*****	1.78	1.87	1.84	1.97	2.44	2.11
% Total Acetylatable as Glycerol	83,44	83.39	84.04	83.80	84.06	83,85	83.8	83.2	83.65	83.98	84.47
% Acetylatable in Residue	0.76	0.43	0.57	0.37	0.46	0.40	0.4	0.3	0.43	0.84	0.80
% Glycerol Corrected	82.68	82.96	83.47	83.43	83.60	83.45	83.4	82.9	83.22	83.14	83.67
% Moisture by Fischer Method	5.07		4.99	******		*******		*****	5.07	5.02	•••••
% Glycerin by Periodic Acid		85.1	81.91				83.6	83.7	84.94	83.26	

Member	8	9			10			A	Standard	Number
Mem ber	A	A	A	В	C	1)	Е	Average	Deviation	of Analyses
Laboratory Analysis										
% Ash	9.33	9.20	9.10	9.37	9.05	9.08	9.13	9.10	0.19	18
% Total Alkalinity as Na ₂ ()	0.81	0.80	0.78	0.72	0.78	0.74	0.79	0.78	0.04	15
% Free Caustic Alkalinity, as Na ₂ O	0.02	0.031	0.016	0.015	0.023	0.03	0.02	0.018	0.007	15
% Carbonate Alkalinity as Na2O	0.05	0.18	0.09	0.05	0.055	0.01	0.04	0.057	0.039	15
% NaCl	7.04	6.95	6.85	7.12	7.04	6.80	7.09	7.03	0.14	18
% Alkalinity Comb. with or Equiv. to Organic Acids	0.74	0.59	0.67	0.66	0.71	0.70	0.73	0.71	0.05	15
% Total Residue at 160°C	10.65	9.95	9.50	11.02	9.81	9.16	10.56	10.52	0.66	17
% Organic Residue at 160°C		0.75	0.40	1.65	0.76	0.08	1.43	1.42	0.64	17
% Total Acetylatable as Glycerol	83.5	82.98	83.70	83.16	83.20	82.88	83.44	83,59	0.41	18
% Acetylatable in Residue	0.5	0.61	0.20	1.07	0.00	0.00	0.23	0.47	0.27	18
% Glycerol Corrected	83.0	82.37	83.50	82.09	83.20	82.88	83.21	83.12	0.41	18
% Moisture by Fischer Method	5.55	5.30	5.15			•••••	*****	5.16	0.18	7
% Glycerin by Periodic Acid	84.3	83.62	84.35				*****	83.98	0.93	10

size sample has been selected. When the sample contains less than 10% glycerol, the range of the glycerol content of the sample tested may be extended to between 0.1000 and 0.1650 gram.

Glycerol, gram
$$= (S - B) \times N \times 0.09209$$

The excess periodic acid is determined as follows: Transfer the blank and sample, after the final titration, to 500-ml, volumetric flasks and fill to the mark with distilled water. Mix thoroughly and pipet a 50-ml, portion of each into 250-ml, wide mouth Erlenmeyer flasks. Add 50 ml, of distilled water, 20 ml, of 15% KI solution, 5 ml, of IICl (sp. gr. 1.19) and mix thoroughly by shaking. Titrate the iodine with 0.1 N $Na_2S_2O_3$ soln, using starch indicator. The sample titration \times 100 divided by the blank titration must be more than 80%."

Acetic Anhydride-Pyridine Method

The acetic anhydride-pyridine method of analysis (2) was tested on samples "B," "C," and "E." The results were not encouraging and the committee voted against further consideration of this procedure.

Standard Crude Glycerin

About 1929, the A.O.C.S. Glycerin Analysis Committee, under the leadership of A. K. Church of Lever Brothers Company, prepared a standard crude glycerin of accepted analysis for use by the industry. The usefulness of this sample for checking purposes was so apparent that the number of samples in the office of the Secretary became depleted to the vanishing point a number of years ago. It was thought advisable to prepare and standardize a fresh supply.

Sample "B" represents a fair quality salt crude glycerin which was allowed to settle for several months to eliminate the difficulty in sampling caused by formation of a slimy deposit on the bottom of the container. Every precaution was taken to insure each bottle being representative of the entire lot. All of the analyses usually made in order to evaluate quality of crude glycerin were made on this sample.

Several members volunteered to submit this sample to other laboratories in their organizations which perform such analyses regularly. This cooperation enabled the participation of up to 18 skilled analysts in the more important tests, or nine more than the

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Sample "C"--Commercial C. P. Glycerin

Member	1	2	3	4	5	6	7	8	9	10	Average	Standard Deviation	Number of Analyses
aboratory Analysis						i		i					
% GlycerinPeriodic Acid Method	96.12	95.65	96.01	96.0	95.6	96.71	96.64	96.9	95.56	96.80	96.20	0.50	10
% Glycerin from Sp. Gr	95.63	95.88	95.86	96.09	95.85	95.85	95.90	95.8	95.70	96.00	95.86	0.13	10
Dichromate		• • • • • • • • • • • • • • • • • • • •	*******		95.5	ا سرسیبر	95.25			*******	95.38	******	2
Gross Acetin	94.57	******	********	•••••	94.4	95.07			93.96		94.50	0.40	4
% Moisture	4.26	******	4.10	4.33	4.0	4.18	4.08	4.2	4.60	4.19	4.22	0.16	9

	Sampi	, D —	Dan I II	AS Added	u Grycer	111 111 44	ater boi	ullon					
Laboratory Analysis							i					-	
% Glycerin—Periodic Acid Method Dichromate		0.171	0.17		0.17	0.17	$0.17 \\ 0.17$	0.17 0.17	0.185	0.179	$0.174 \\ 0.17$	0.005	9 2
Gross AcetinPermanganate			0.15			•			0.18	•••••	0.15 0.18		1
% NaCl.	16.33	16.77	16.85		17.0	16.81	16.63	16.5	16.93	16.82	16.74	0.20	9

Member	1	2	3	5	6	7	8	9	10	Average	Standard Deviation	Number of Analyses
Laboratory Analysis					i			1				
% Ash	1.07	0.99	1.10	1.3	1.13	1.14	1.12	1.20	1.18	1.14	0.082	9
% Total Alkalinity as Na2()	0.090	0.054	0.05	0.12	0.02		0.03	0.050	0.08	0.06	0.031	8
% Free Acidity	0.035	0.034	0.03	0.015	0.03	0.04	0.03	0.057	0.04	0.035	0.011	j 9
% NaCl	0.022	0.058	± 0.12	0.12	0.11	0.09	0.15	0.16	0.12	0.106	0.041	9
% Alkalinity Comb, with or		1	1]	1	ì	ì	1)	Ĭ	ì	Ì
Equiv. to Organic Acids	0.125	0.142	0.14	0.103	0.16	0.16	0.20	0.19	0.14	0.15	0.029	9
% Total Residue at 160°C	1.44	1.74	1.60	1.80	2,05	2,30	1.91	1.98	1.62	1.83	0.25	9
% Organic Residue at 160°C	0.38	0.75	0.50	0.53	0.92	1.16	0.79	0.78	0.71	0.72	0.22	9
	87.96	88.58	88.66	87.8	88.14	88.34	87.6	87.99	88.13	88.14	0.33	9
% Acetylatable in Residue	1.13	[-0.12]	0.34	0.3	0.28	0.56	0.2	1.26	0.37	0.51	0.39	9
% Glycerol Corrected		88.46	188.32	87.5	87.86	87.78	87.4	86.73	87.76	87.63	0.56	9
% Moisture by Fischer Method	9.45		9.33		9.51	9.23	9.7	9.90	9.99	9.59	0.27	7
% Glycerin by Periodic Acid	89.0 6	90.9	189.75	88.2	89.56	87.90	89.1	88.53	89.93	89.21	0.88	9

A.O.C.S. GLYCERIN ANALYSIS COMMITTEE 1947-1948 Sample "E"-Saponification Crude Glycerin

present membership of the committee. The arithmetical mean, or average, has been computed for each analysis from the data reported, also the stand-

ard deviation
$$\left(\sqrt{\frac{\Sigma d^2}{N}}\right)$$

This value is a measure of the reproducibility of the test by analysts of the same degree of skill, in this case in different laboratories. In any one laboratory with a single analyst, the standard deviation would be expected to be considerably smaller. Particularly important are the standard deviations for "% Total Acetylatable as Glycerol" and "% Glycerol Corrected" which, by coincidence are both 0.41. This value is almost identical with that calculated from data given in previous reports of the Glycerin Analysis Committee (3), which was 0.4.

These analyses are not advanced by the committee as absolute and final. They represent accepted values, obtained by our official methods, in laboratories regularly engaged in such work, by analysts of such skill and experience that they are typical of what may be expected on crude glycerin from which the error in sampling caused by non-homogeneity has been eliminated.

The Glycerin Analysis Committee recommends that sample "B" be accepted by the American Oil

Chemists' Society as a standard crude glycerin for distribution by the Secretary. We further recommend that a certificate of analysis be included with each bottle sold, showing the average values for the first 12 items in the table, with a reference to the appropriate A.O.C.S. method for each analysis. About 250 4-oz. bottles of this sample are available.

Future Work

The committee has planned a program of further study of the acetin and periodic acid methods on crude and distilled glycerins in the hope that the latter procedure may be improved to such an extent that it may eventually become our official method for the chemical analysis of glycerin.

REFERENCES

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GLYCERIN ANALYSIS COMMITTEE-1947

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The 1948 committee includes the same personnel as above with the exception of Mr. Van Zile.