TABLE IV
Performance Data on Nitrile Rubber Compositions Containing Experimental Plasticizers

Plasticizers	300% Modulus, p.s.i.		Ultimate tensile strength, p.s.i.		Ultimate elongation, p.s.i.		Brittle point, °C.
	Unaged	Aged[a]	Unaged	Aged	Unaged	Aged	
Controls							
None	2970	......	3380	3420	400	210	−32
Polymeric epoxy	1420	......	2950	3110	600	260	−26
Petroleum type	1670	3210	3020	3300	550	310	−28
Di-2-ethylhexyl sebacate	1650	3300	3190	3410	530	210	−32
Linoleic adducts							
Trimethyl ester of maleic adduct	1620	3180	3100	3360	560	335	−27
Dimethyl ester of acrylic adduct	1480	2970	3170	3110	600	320	−32
Epoxidized dimethyl ester of acrylic adduct	1380		3130	2880	620	340	−29
Oil adducts		2740					
Safflower dibutyl maleate adduct	1510	2800	2430	2980	490	320	−18
Linseed dibutyl maleate adduct	1620	2830	2570	2830	500	310	−29

[a] Aged in metal block heater at 212°F. for 7 days.

TABLE V
Rating of Most Promising Adduct Products as Plasticizers for Nitrile Rubber

Plasticizer	Relative rating index[a]					
	Efficiency	Compression set	Volatility	Extraction		Brittle point
				ASTM oil No. 1	Ref. fuel B	
Controls						
None	10	4	11	16	4	1
Polymeric epoxy type	2	10	10	17	9	6
Petroleum type	5	2	13	15	10	4
Di-2-ethylhexyl sebacate	3	1	14	6	6	1
Linoleic adducts						
Trimethyl ester of maleic adduct	3	1	3	8	2	5
Dimethyl ester of acrylic adduct	2	1	9	11	1	1
Epoxidized dimethyl ester of acrylic adduct	1	6	9	1	3	3
Oil adducts						
Safflower dibutyl maleate adduct	4	3	2	2	16	9
Linseed dibutyl maleate adduct	5	8	4	12	15	3

[a] Best = 1.

good compatibility with acrylonitrile synthetic rubber. The remaining four, which included the epoxidized tri-2-ethylhexyl ester and the tri-*n*-butyl ester of the maleic adduct and the epoxides of the di-2-ethylhexyl ester and the di-*n*-butyl ester of the acrylic adduct, were only partially compatible. All of the vegetable oil adduct esters and epoxides showed good compatibility. As judged by appearance and feel of the specimens, compositions plasticized with the vegetable oil adduct products were "drier" than some plasticized with compatible linoleic adduct esters and epoxides. Performance data and relative rating indices for the more promising experimental plasticizers are given in Tables IV and V. It is evident that the experimental plasticizers compared favorable to the control plasticizers. The dimethyl ester of the acrylic adduct equalled or exceeded any of the controls.

Considered as a group, the vegetable oil adduct esters and their epoxides were generally similar in performance to the petroleum type of control except that they were less volatile and less readily affected by ASTM oil No. 1. The lowest brittle point was observed with the linseed dibutyl maleate adduct.

All of the plasticizers tested, both experimental and control, showed approximately equivalent behavior in tests for contact and migration staining.

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Water Absorption of Soybeans

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The rate of water absorption of U.S. and Japanese soybeans has been measured at 10° and 25°C. and at initial moisture levels ranging from 7.5 to 14.0%. The principal controlling factor in absorption of water is the seed coat. However the rate of water absorption of sound whole beans is also influenced by the initial moisture level in the beans; the lower the moisture the slower the rate of water absorption. The presence of hard beans also reduces the rate of water absorption. U.S. soybeans usually have lower moisture and contain more hard ones than do Japanese beans. These factors are attributed to the climatic differences of the two countries. No fundamental differences were found in the rate of water absorption of U.S. and Japanese soybeans.

THE RATE OF WATER ABSORPTION of soybeans is controlled by their seed coat; a pinhole or a crack in the coat greatly increases the absorption rate.

Brown, Stone, and Andrews (2) of the Tennessee Agricultural Experiment Station described a labo-

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[1] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

ratory method and equipment for cracking the seed coat of soybeans and other seeds, thereby increasing the rate of water absorption. They treated seeds in a closed system with an electrical potential sufficient to produce a glow discharge in a tube at a pressure of about 1.0 mm. of mercury. After this treatment soybeans absorb water very rapidly.

Seeds treated by this method of irradiation were supplied to us by the Tennessee workers and were examined under a microscope by M. J. Wolf, histochemist at the Northern Regional Laboratory. He reported that "in the coat of the treated seeds a characteristic, branched checking and cracking was observed. In most beans this type of damage covered the entire area of the seed coat or a large part of it. The checks appeared white, indicating presence of air; sometimes the checks were actual cracks in both seed coat and cotyledon, clearly open to the exterior of the seed."

Hard Soybeans

When soaking beans in water, one finds a variable number which have unusual resistance to absorption of water; such beans are called "hard beans." For practical reasons hard beans are defined here as those that do not absorb enough water in 16 hrs. to soften normally when cooked in steam. Usually hard beans can be easily identified after being in water for a few hours because of their small size and firmness.

The slow rate of water absorption of hard beans, like normal beans, is controlled by the seed coat. Any mechanical treatment which cracks the seed coat or makes a pinhole will permit rapid water absorption. Handling, transportation, and storage under variable conditions of temperature and moisture tend to fracture the seed coat and to reduce the number of hard beans. Thus, by the time soybeans reach their destination in Japan, the number of hard beans should be greatly reduced. Also, because they are usually small-sized beans, many can be removed with a grading screen.

Hard beans are well known to people who test seeds for germination as their slow rate of water absorption also retards germination. Soybeans from any source may contain hard beans, but it appears from our tests that they occur more frequently in the U.S. than in Japanese beans. J. L. Cartter (3) of the U.S. Soybean Laboratory has stated that the development of hardness is partly the result of hot and dry weather during the ripening period and therefore is more of a climatic than a varietal factor.

The number of hard beans and their degree of hardness as measured by water absorption vary and cannot be accurately counted.

We found that the number which is counted in a sample varied with their moisture content. For example, a 100-g. sample of beans at a moisture level of 7.6% contained 85 hard beans after soaking in water for 24 hrs. Beans from this same sample were adjusted to a moisture of 13.8%, and the soaking test was repeated. The number of hard beans in the 100-g. sample was reduced to 6. On permitting the sample to dry out again to a low moisture, most of the hard beans reappeared.

Preliminary experiments were made on U.S. and Japanese beans stored for several months under the same conditions of humidity and temperature and thus contained essentially the same amount of moisture (1). Test results with these beans did not show any significant differences in the rate of water absorption. Because Japan is a country of high humidity, their soybeans usually contain higher moisture than ours. Many Japanese soybeans are known to contain 14 to 15% moisture whereas U.S. soybeans will lose moisture down to 10% or even lower, depending on storage conditions. With these climatic conditions and others in mind, a series of water-absorption tests were made, using soybeans at different initial moisture levels.

Experimental

Sound, whole soybeans were hand-selected for water-absorption tests. This method of selection eliminated broken beans and ones with cracked or otherwise damaged seed coats. It is realized that some beans with invisible cracks in their seed coats may have passed the screening test and affected results to an unknown extent. Also there is no correction for the hard beans present in the various samples although some of them were probably eliminated in sorting. Because of these unmeasured factors the results are regarded as not having any particular degree of precision, but they are considered adequate for the conclusions discussed later.

The rate of water absorption was determined on 100 g. of beans. The samples were corrected for moisture content so that the results show water absorption on a dry-bean basis. The beans were placed in a loose mesh, plastic bag, and the bag was placed in a 600-ml. beaker of water held in a constant temperature bath. The bags were removed each hour, drained for ½ min., weighed, and returned to the bath. Weighings were made usually each hour for the first 7 hrs., and a final weighing was made at 24 hrs.

Measurements were made at 10° and 25°C. and at initial moisture levels ranging from 6.4 to 14.5%.

During the winter months the moisture of beans in our laboratory fell below 7%. To raise their moisture level the beans were placed in a closed container with a saturated solution of potassium bromide that permitted a relative humidity of 84% at 20°C. At these conditions about 5 months were required to raise the moisture from 6.5% to above 13.0%. A humidity of 95% was tried, but when the moisture rose above 13.0%, a mold appeared on the beans.

Moisture determinations were made on a Steinlite moisture meter which had been standardized against oven moisture values made in a forced-draft oven at 130°C. for 3 hrs.

Results and Discussion

Table I shows the rate of water absorption for U.S. soybeans at 25°C. and various initial moisture levels

TABLE I

Water Absorption by U.S. Soybeans at 25°C. and Five Different Initial Moisture Levels

No. varieties tested	6	3	3	4	5
Moisture range %	6.5–6.8	7.0	8.0–8.4	12.4–12.8	13.1–13.7
Avg. moisture %	6.62	7.0	8.3	12.6	13.6
Soaking time (hrs.)	Water absorbed, g./100 g. soybeans				
1	66	67	73	71	70
2	85	87	93	96	92
3	101	103	108	112	115
4	116	117	119	128	135
5	126	128	131	140	145
6	135	137	140	149	153
7	144	145	145	157	159
24	167	166	160	169	170

TABLE II

Water Absorbed by Japanese Soybeans at 25°C. and Different Moisture Levels

Variety	Hokkaido [a]	Aomori [a]	Hakuho	Average	Miyagi	Hokkaido	Aomori	Average
Initial moisture in beans, %	6.5	6.8	6.9	6.7	13.1	14.2	14.7	14.0
Soaking time (hrs.)	Water absorbed, g./100 g. soybeans							
1	59	58	45	54	67	67	65	66
2	77	76	64	72	90	84	87	87
3	90	93	80	88	112	100	109	107
4	104	112	92	103	130	119	127	125
5	112	125	102	113	143	137	141	140
6	124	135	113	124	154	150	150	151
7	134	144	119	132	161	162	156	160
24	180	175	176	177	177	179	171	176

[a] Contained four hard beans per 100 g.

from 6.6 to 13.6%. Corresponding data for Japanese beans appear in Table II. Data in Table I are average values of several varieties at each moisture level whereas Table II contains values for single samples as well as their averages. The averages are made up from samples that had moisture levels within a range of a few tenths of 1%. Table III shows the water absorption rates at 10°C. for both U.S. and Japanese beans.

The initial moisture content of the beans is a factor in the rate of water absorption for a period somewhat longer that 7 hrs.; beans with high moisture absorb water more rapidly than those with low moisture.

Table IV shows the water absorbed after 24 hrs. in grams of water per 100 g. of beans and also moisture calculated on the weight of wet beans, respectively. After 24 hrs. the effects of the initial moisture level appear to be lost; however we are not certain that a moisture equilibrium was reached. Equilibrium is not easily measured since, after 24 hrs. in water, there is a nonuniform leaching of bean constituents, perhaps promoted by enzyme activity. However, if the 24-hr. results are assumed to represent moisture equilibrium, it appears that Japanese beans took up about 11 g. more water per 100 g. of beans than did U.S. beans; this small difference has aroused some speculation as to its cause.

Protein and insoluble carbohydrates are the components primarily responsible for absorption of water. In isolating soybean protein we have found that, under similar physical and chemical conditions, the residue of the extraction, which is about 65% water-insoluble carbohydrate, holds 10 times its weight of water whereas the extracted protein holds only twice its weight. Although the physical state of the protein and of the carbohydrates after extraction differ from what they are in the whole bean, it is believed that their relative water-absorbing capacity may be much the same. An earlier report (7) shows that the average protein in Japanese soybeans is only about 1% greater than in U.S. beans and thus could not account for the difference in absorbed water. It seems more likely that the difference should be attributed to a possible difference in water-insoluble carbohydrates.

TABLE III

Water Absorption at 10°C. by U.S. and Japanese Soybeans at Two Moisture Levels

	U.S. soybeans		Japanese soybeans	
No. of varieties tested	5	4	4	4
Moisture range %	6.4–7.0	12.3–13.5	6.4–6.8	13.6–14.2
Avg. moisture %	6.5	13.1	6.6	14.0
Soaking time (hrs.)	Water absorbed, g./100 g. soybeans			
1	51	60	44	51
2	70	78	62	68
3	82	91	74	78
4	93	103	87	89
5	102	113	97	98
6	109	121	107	106
7	121	131	120	115
24	163	168	178	170

The development of mechanical equipment for scratching or breaking the seed coat of a soybean would seem to be a logical way to increase the rate of water absorption. However for food products like natto and hamanatto the problem is complicated by other requirements.

TABLE IV

Average Water-Absorption Values of Soybeans, Having Various Moisture Levels, After Soaking 24 hrs. in Water at 25° and at 10°C.

Taken from table	No. of varieties	Initial average moisture	Temp. of absorption	Water absorbed in 24 hrs.	Moisture in whole beans after 24 hrs.
U.S. soybeans					
	avg.	%	°C.	*g.*	%
1	6	6.6	25	167	62.6
1	3	7.0	25	166	62.4
1	3	8.3	25	160	61.5
2	4	12.6	25	169	62.9
2	5	13.6	25	170	63.0
Avg.	....	....	....	166.4	62.3
3	5	6.5	10	163	62.0
3	4	13.1	10	168	62.8
Avg.	....	....	....	165.5	62.4
Japanese soybeans					
2	3	6.7	25	177	63.9
2	4	14.0	25	176	63.8
Avg.	....	....	....	176.5	63.9
3	4	6.6	10	178	64.0
3	4	14.0	10	170	63.0
Avg.	....	....	....	174.5	63.5

Natto and hamanatto are made by fermenting whole beans, and how the whole bean looks in the final food product is an important factor in customer acceptance. The glow-discharge method causes such a large number of cracks that when beans are soaked in water many of the hulls loosen and break away from the cotyledons; the loose hulls give the final product an unsatisfactory appearance. Mechanical scratching of the seed coat, as with sandpaper, would be another method expected to increase the rate of water absorption, but this treatment dulls the seed coat and produces a less acceptable product. Thus the mechanical pretreatment of beans to improve water absorption for making natto and hamanatto does not seem feasible.

Breaking the seed coat would not be objectionable in making miso, the most important of the fermented food of the Japanese made from whole beans, because the final step in processing is to grind miso into a thick paste. However recent research at the Northern Laboratory developed a different approach to this problem of nonuniform water absorption for making miso. The new method (5) makes an improved quality of miso in a shorter fermentation period than the old method by using dehulled soybean grits which absorb water and which cook rapidly and uniformly. If the new method of making miso is adopted, the problems of water absorption and cooking will be eliminated in the miso process.

Acknowledgment

This work is part of a program at the Northern Regional Research Laboratory on the use of U.S. soybeans in foreign markets. The study on water absorption of soybeans was undertaken in part as a result of a special survey made in Japan by one of us (A.K. Smith) (6) and subsequent joint studies (4,5,7, and other proposed publications) at the Northern Laboratory sponsored by the American Soybean Association, Hudson, Ia., and the Foreign Agricultural Service and Agricultural Research Service of the U.S. Department of Agriculture. The samples of Japanese beans were supplied by the Japanese-American Soybean Institute.

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Removal of Fatty Soil from Glass by Surfactants and Surfactant-Builder Compositions[1]

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Previous papers have reported radiotagged fatty soil removal from glass either by solvents or by aqueous solutions of sodium tripolyphosphate and other builders. This paper provides soil-removal data for aqueous systems of both pure and built surfactant compositions of the nonionic and alkylbenzene sulfonate types. In general, nonionics are the most effective detergents for the system fatty soil/glass; the 10-mole ethylene oxide adduct products show peak soil-removal. Nonionic surfactants appear most effective for soil removal when used in baths closely approaching their cloud-points. Though modification of hydrophobe by EO addition can affect cloud point, peak soil-removal effectiveness seems to be controlled by hydrophobe selection. Highest soil removal for the alkylbenzene series occurred with the longer alkyl chain (pentadecyl).

Admixture of surfactant and sodium tripolyphosphate provided synergistic compositions with certain 10-EO surfactants. Building of anionics markedly improved soil removal over the pure material but seldom exceeded the removal by STP alone.

PREVIOUS DATA (1,2) developed in the removal of radio-tagged tristearin from a glass substrate showed that the initial removal of cohesively-bound soil could be by dissolution if a solvent were used, and probably by emulsification if an aqueous medium not a solvent for fat (sodium tripolyphosphate solution) were used. Removal of adhesively-bound soil is more difficult than for that cohesively held, and the mechanism appears to be one of preferential displacement of soil by a more polar substance, which releases the soil from adsorption sites. In the solvent systems the more polar the solvent, the greater was the ease and completeness of soil removal. In the aqueous sodium tripolyphosphate removal system, preferential soil displacement was the significant mechanism.

The present paper is concerned with fatty soil removal in aqueous systems by a variety of surfactants and surfactant-builder compositions.

Experimental

With the exception of the following details the procedure was the same as that previously described (1,2). In addition to carbon-14 tagged tristearin, carbon-14 tagged triolein was used in certain experiments. In all cases spotted soil applications were used, as indicated in the figures. Wash temperatures are likewise indicated.

The nonionic surfactants were laboratory preparations from which the catalyst had been removed. The alkylbenzene sulfonates and the other anionics were essentially 100% active ingredient obtained by purification. The alkylbenzenes were cuts corresponding essentially to the carbon chain-lengths noted; sodium oleate and sodium lauryl sulfate (U.S.P.) were obtained from the Fisher Scientific Company.

Nonionics. The effect of molar ethylene oxide (EO) ratio at constant solution concentration upon soil removal is shown in Figure 1. Peak removal occurred at a 10-molar EO level, and while this curve is for n-dodecanol, similar curves were obtained for other adducts.

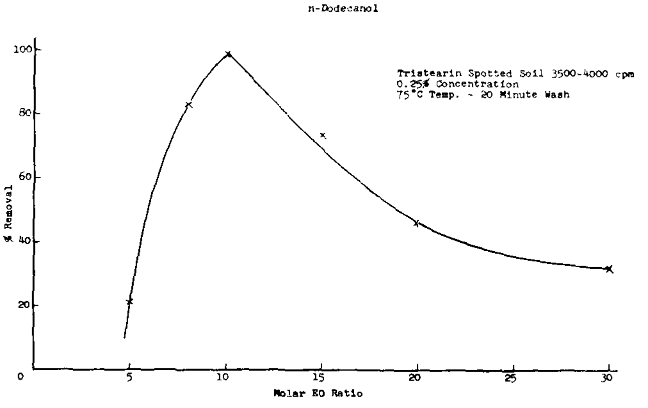

FIG. 1. Effect of Molar EO ratio on detergency.

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[1] Presented at 34th fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.