New Household Detergent Based on AOS[1]

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Abstract

The synthetic detergent industry is one of the fastest growing industries in Japan. Its production, together with soap, is estimated to be almost 2 billion pounds in 1970. In addition to this increased production, quality modification in terms of biodegradability is now being undertaken. Alpha olefin sulfonate (AOS) has been known since the 1930's, but only within the last two years has it been highlighted for commercial interest as a detergent material due to progress in sulfonation technology as well as commercial availability of alpha olefins. To make use of AOS as an active ingredient for formulation of heavy duty household granules, several properties of AOS itself or of the built detergent were studied in comparison with linear alkylate sulfonate (LAS), alkylbenzene sulfonate (ABS) and alcohol sulfate (AS). AOS was proved to be a potentially economical detergent material having as good performance and better biological properties than LAS or AS and better biodegradability than LAS. It has been marketed since 1967 in Japan as the first AOS-based household heavy duty granular detergent. It has been accepted by the housewives as the most efficient detergent and has become the best selling brand.

Introduction

The volume and value of the detergent industry in Japan is constantly increasing. Total production including soap in 1970 is estimated to be 1.95 billion pounds, of which synthetic detergents will be 82%; toilet soap bars, 12%; and other soaps, 6% as shown in Figures 1 and 2. The yearly increase between 1965 and 1970 is estimated to be about 11%, and per capita production in 1970 may grow to 18.6 lb. from 11.9 lb. in 1965.

Along with this volume increase, raw materials for detergent manufacturing are and will be changing due to the trend to more biodegradable detergent formulations. So far, alkylbenzene (AB) has been the only major material for detergent active ingredient, and detergent alcohol (A) has trailed far behind. The major outlet for alcohol sulfate (AS) until the mid-1960's was for wool washing both for household and industrial use.

When the switchover to biodegradable detergents took place in Germany and the United States during 1964–1965, the same movement occurred in Japan, initiated at first by local detergent manufacturers in early 1965 and followed by the major manufacturers. In the second quarter of 1967, domestic production of linear alkylate (LA) started, and the voluntary change to biodegradable detergents became more active. Figure 3 shows this change of materials especially between 1965 and 1967. First, new active materials such as LA and alpha olefin (AO) appeared; and the use of alcohols increased steeply in 1967. Thus, a diversity of active ingredients developed in detergent formulations. Second, the increase of detergent production was about 140%; but the material increase for actives (LA, AO, AB and A) was only 120%. This may indicate a decrease of active level in the detergent formulation as has been observed already in the United States. Finally, the content of phosphate builder in relation to active ingredient was increased in 1967 and will continue to increase in the future. Figure 4 shows production capacity for detergent alkylate and alcohol, in which alcohol capacity includes all fractions, with the detergent fraction estimated to be two thirds of the total.

As mentioned above, marketing of biodegradable detergents was started in 1965. By law in Germany, and voluntarily in the United States, this switchover was programmed to start simultaneously by all detergent manufacturers; in Japan each manufacturer changed by himself, brand by brand. Apart from this marketing activity, discussions on biodegradability related to the water pollution problem had already been held in 1963, and the officially organized Synthetic Detergent Committee started its first meeting in early 1965. This committee was set up as one of the advisory functions within the Ministry of International Trade and Industry (MITI). The members for this committee were appointed by the Government in mid-1964. Early in 1967 the committee submitted a report to MITI recommending the biodegradability target as follows: over 80% by 1968 and over 85% by 1970 or as soon as possible thereafter. This recommendation was accepted by MITI, and the chief of the Chemical Industry Bureau asked the manufacturers to cooperate to assure achievement of these goals.

The Testing Method for Biodegradability of Synthetic Detergents was published as Japan Industrial

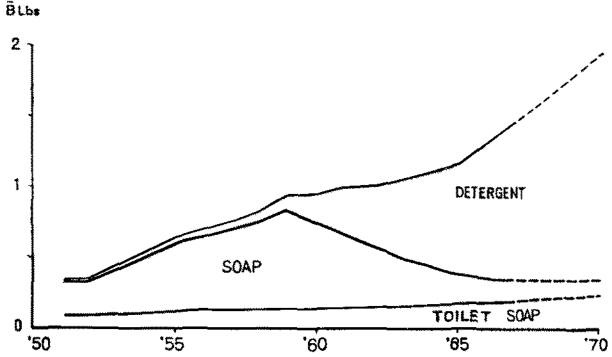

FIG. 1. Soap and detergent production.

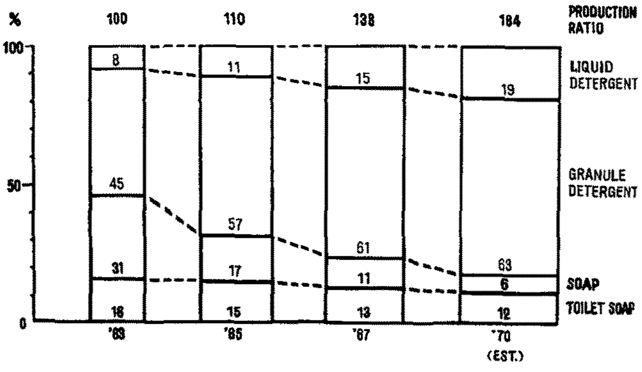

FIG. 2. Soap vs. detergent.

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[1] Presented at the AOCS-AACC Joint Meeting, Washington, D.C., April 1, 1968.

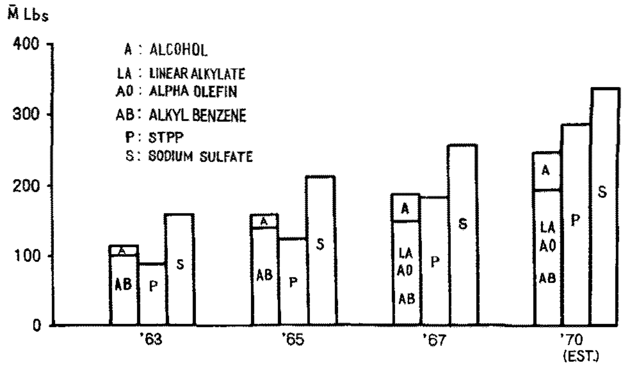

FIG. 3. Raw materials consumption for detergent.

Standard (JIS) on April 1, 1967. This is the authorized test method for discussions on biodegradability standards in Japan. Figure 5 illustrates the timing and estimates average biodegradability. In the course of this debate, several new candidates were proposed or introduced as biodegradable detergent actives, but from the standpoint of economics, only linear alkylate and detergent alcohol were readily acceptable to the detergent industry as was the case in Europe and the United States. Lion has been manufacturing ABS since 1950. Along with the expansion of detergent production, the sulfonation process has been improved from the old batch system through continuous to a thin film sulfonation system. There was also a change from oleum to SO_3 as the sulfonating agent. As for material to be sulfonated, there was no change from alkylbenzene which contains the aromatic ring to make sulfonation feasible.

In view of this we have been looking for new raw materials which contain no benzene ring but are sulfonatable by new sulfonation technology which should be commercially applicable in our plants. Alpha olefin is, of course, one of these and was studied in the early 1960's, but due to a lack of commercial or economical availability of alpha olefins at that time, no concrete progress was made. Commercial production of alpha olefins was on stream in late 1965 by the two United States firms which encouraged us to reinvestigate these olefins for commercial development of AOS as a biodegradable detergent in Japan.

As shown in Figure 5, early 1966 was just the time every detergent manufacturer in Japan was absorbed in developing a biodegradable detergent. After less than one year of development work, we were convinced of two points: (a) AOS was quite competitive in quality to LAS or AS as the active material for household detergent formulations; and (b) utilization of the higher fraction AO–C_{14} or C_{15}–C_{18} in bulk usage for detergents would assure economical establishment of wax cracking or ethylene polymerization processes for AO. This, in turn, would contribute to the petrochemical industry by offering a new product series of AO chemicals, and would give AO enough potential to reduce its cost to a level competitive with the other chemicals mentioned above.

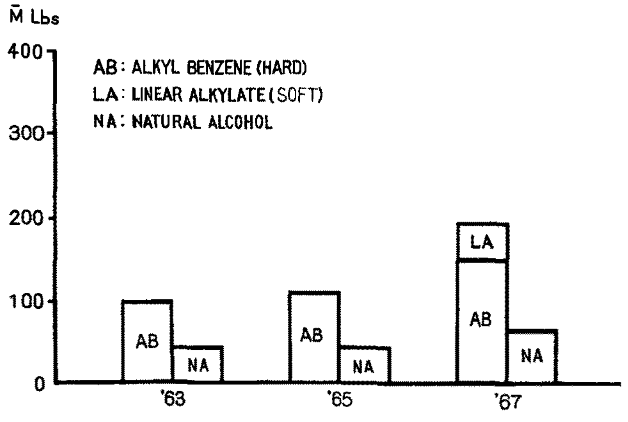

FIG. 4. Capacity of detergent alkylate and alcohol (alcohol capacity includes lower fraction).

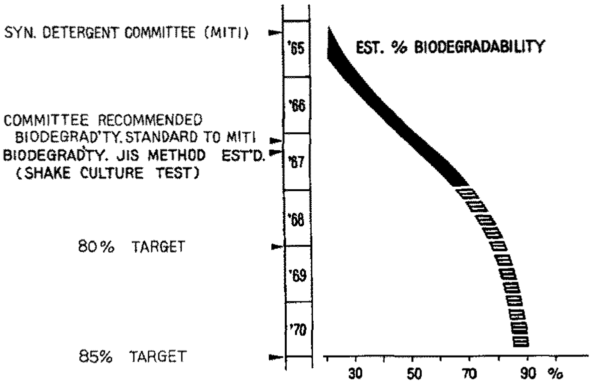

FIG. 5. Switch-over to biodegradable detergent in Japan.

One of the major concerns in marketing an AOS-based detergent was storage stability of the final product through wholesaler and retailers. In Japan there are very sticky conditions due to two rainy seasons in summer when humidity is often more than 95% and the temperature is above 35 C. During last summer we carefully watched the new product on the shelves of retailers and confirmed that no fatal damage was observed. The new product received a very good reputation with housewives in all respects and became the major best selling brand quite promptly.

Fundamental Detergent Properties of AOS

Sulfonation

Sulfonation of AO is rather complicated compared with other conventional materials such as LA, AB or A as already reported or reviewed by many authors (1–3). One significant difference from a conventional material such as LA in gaseous SO_3 sulfonation of AO is that acidic or alkaline hydrolysis is necessary after sulfonation because water-insoluble or nonsurface active sultones are formed and remain after the sulfonation reaction. Figure 6

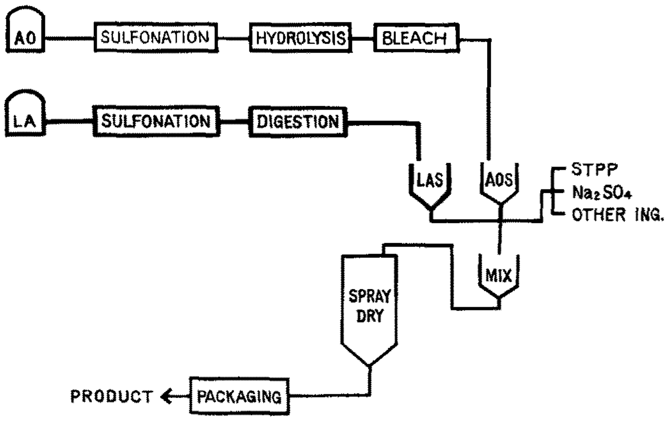

FIG. 6. Process flow.

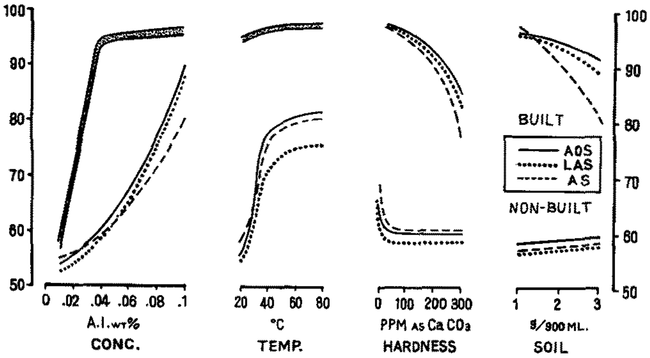

FIG. 7. Detergency of AOS, LAS and AS built and non-built formulation.

describes the detergent manufacturing process flow briefly.

Raw Materials

Active materials used in this report are tabulated in Table I which shows AO made by wax cracking, and A derived from cocoanut oil. The inorganic or organic builders or additives used in the formulations are all commercial products.

Detergent Properties

Detergency, foam height and storage stability of AOS, LAS, ABS and AS are compared as both built and unbuilt detergent formulations. In this paper an unbuilt detergent formulation means the active ingredient itself. The experimental formulation of built detergent is 20% active ingredient, 30% sodium tripolyphosphate, 5% sodium silicate and 10% water. The difference is balanced by sodium sulfate and small amounts of carboxymethylcellulose and antitackiness agent. Artificial soil and natural soil are used for detergency measurements. The artificial soil composition is a mixture of sebum soil, clay and carbon. The sebum soil is a modification of the one given by Spangler (4). Details of the detergency test method using artificial soil composition will be reported separately. The standard washing conditions are active concentration, 0.04%; temperature, 25 C (77 F); hardness, 54 ppm; 1 g of sebum soil in 900 ml of wash solution and 30 g of cloth using the Terg-O-Tometer. Concentration, temperature, water hardness and soil content are varied. Results using artificial soil are shown in Figure 7 where the upper group of curves represents detergency of the built formulation and the lower group indicates unbuilt performance. AOS has slightly better detergency than LAS or AS in the unbuilt system but no substantial difference is observed in the built system except that built AS is poor in the presence of a large amount of soil.

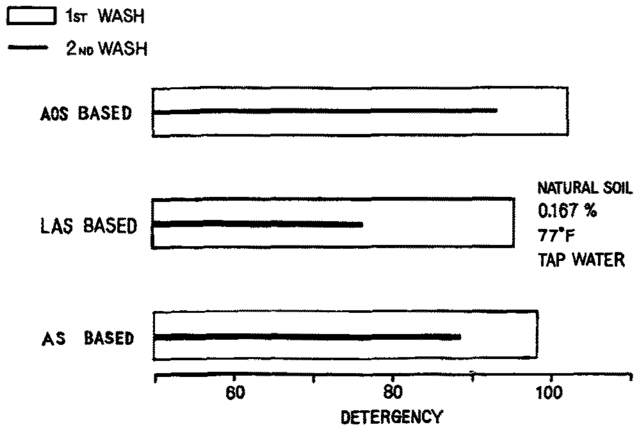

FIG. 9. Detergency of commercial heavy-duty detergents.

Three types of commercial heavy duty detergent were chosen for detergency measurement using naturally soiled cloth. Although the composition of the active ingredient of these three is a mixture of AOS, LAS, ABS or AS, one is designated as AOS-based because AOS is the major constituent with LAS and ABS. The product designated LAS-based contains both LAS and ABS; the AS-based contains AS, LAS and ABS as used in Figures 8 and 9. Since these three are commercial products, the builder formulation is also different in each run, for example, the LAS-based run contains relatively less STPP or silicate than the other two. So the result of detergency does not correlate directly to the type of active ingredient, but AOS is as good an active ingredient for a detergent formulation as the conventional ABS, LAS and AS in terms of detergency. A comparison between detergency of the first and second washes of the same products is shown in Figure 9. In Japan, due to a different mechanism of the electric washer, detergent consumption per unit weight of cloth or fabric is about twice as much as in Western countries. Thus, the detergent solution after the first wash load retains considerable detersive power; and since housewives know this, empirically, they ordinarily wash two times and sometimes even three times with the same detergent solution; we call this the second or third wash. The detergent having the smaller difference of detergency between the first and second washes is preferred by housewives, and the test results in Figure 9 indicate at least that AOS is acceptable in this respect.

The foam height in the beakers of the Terg-O-Tometer in the presence of soiled cloth is shown in

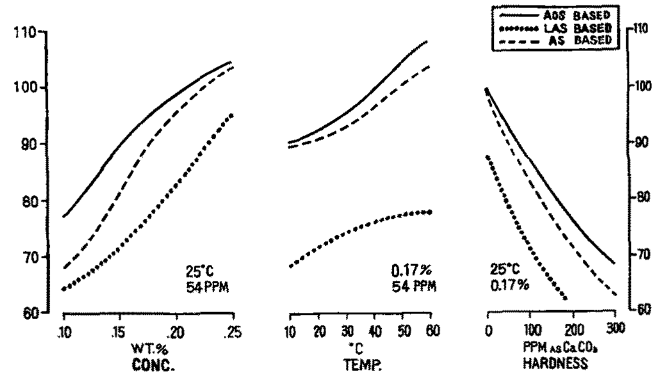

FIG. 8. Detergency of commercial heavy-duty detergents (natural soil).

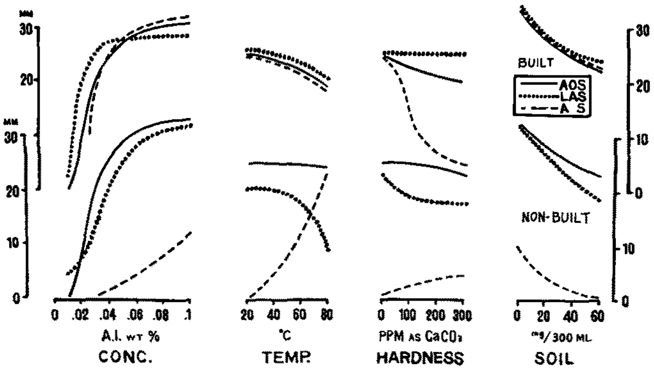

FIG. 10. Foam height of AOS, LAS and AS built and non-built formulation.

TABLE I

Active Materials

	AO	LA	AB[a]	A
Alkyl chain	15~18	10~14	11~15	10~18
Main fractions[b]	15~18	10~13	12	12,14
Mean mol. wt.	228	243	246	204
Oil in sulfonate[c]	2.1	2.0	2.0	2.2

[a] Narrow cut AB.
[b] Fraction over 10%.
[c] Oil per cent based on active.

TABLE II

Biodegradability
Shake Culture Test (JIS K 3363)

Date	AOS	LAS	AS
Sep. '66	99.2%	92.2%	99.6%
Nov. '67	97.1%	90.4%	98.8%

TABLE III

Acute Toxicity
(Mouse Oral Administration, 24 hr)

Sample	n	LD_{50}, g/kg	95% Confidence Limit, g/kg
AOS	10	3.26	2.67~3.98
ABS	10	1.62	1.34~1.96
LAS	5	1.62	1.11~2.35
AS	5	1.46	1.01~2.12

TABLE IV

Acute Toxicity
(Mouse, 24 hr)

	AOS, g/kg	ABS, g/kg	
Oral	3.26	1.62	10% Soln.
Subcutaneous	1.66	0.35	0.1 ml/per
Intraveneous	0.09	0.12	
Intraperitoneal	0.30	0.12	10g Mouse body

TABLE V

Skin Mildness

	Hand Immersion	Upper Arm Patch
Water	0.4	0.8
AOS	0.8	2.0
ABS	1.4	1.9
LAS	(0~5 Rating)	2.0
AS		2.4
Conc.	0.3%	1%
Temp.	35 C (95 F)	....
Duration	(1 min dip and 1 min dry) × 30	24 hr
Observed at	Immediately, 24 & 28 hr	Immediately
Rated on	All 7 symptoms	Erythema & Fissuring
Symptoms	Erythema, fissur'g, papula, vesicle, p. scale, supple, irritation	

TABLE VI

Performance Assessment by Housewives

	Responses, %		
	Better	Same	Poor/ not identified
Detergency	75	20	5
Feeling of washed fabrics	55	30	15

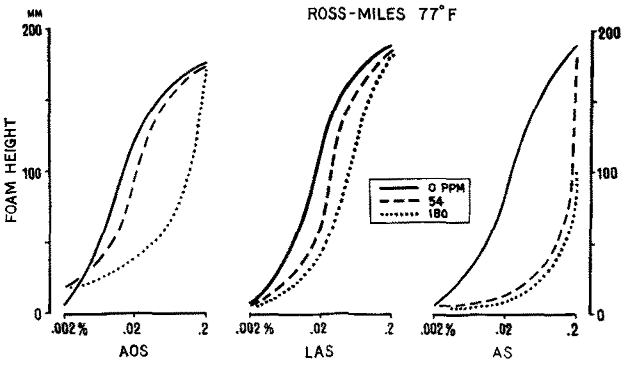

FIG. 11. Foam height of built detergent.

Figure 10. Again, smaller differences are observed in the built system than in the unbuilt system. In general, AOS is good in both systems. The Ross-Miles foam height of built detergent in relation to detergent concentration and water hardness is shown in Figure 11, which indicates hard water performance of AOS is intermediate between LAS and AS.

The storage stability toward caking of a built detergent having a ternary active ingredient system is shown in Figure 12. If the same formulation is applied for all active ingredients or mixtures of them, AOS has a faster tendency toward caking than the others. This problem was solved only after we had carried out extensive formulation studies. LAS or ABS gives fabrics a harsh feeling. Yet a feature of AOS is its property of imparting a soft feeling to washed fabrics as does the alcohol sulfate from spermaceti oil.

Biodegradation

Biodegradability of AOS, LAS and AS by the Japan Industrial Standard test method (a shake culture test modified slightly from the SDA test) has been measured as shown in Table II. The rate of biodegradation has also been measured (Figure 13) and these results put AOS nearer the AS than to LAS.

Biological Properties

The acute toxicity of AOS is significantly lower than that of LAS or AS (Table III) using a 10% solution of each surfactant by oral administration to mice. Subcutaneous intravenous or intraperitoneal administration was also tested to compare AOS and ABS (Table IV). Rabbit eye irritation by our threshold test technique indicates that LAS is two to five times more irritating than AOS or ABS (Figure 14). Skin mildness by immersion and patch tests is sum-

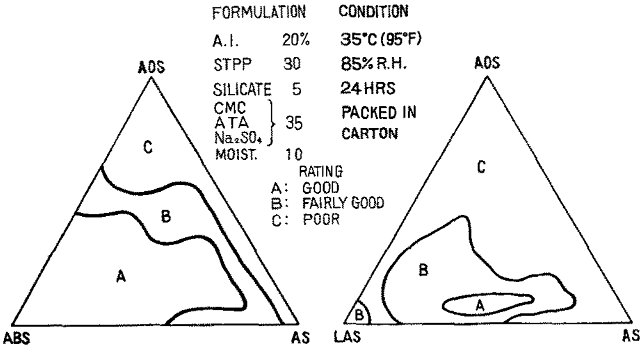

FIG. 12. Storage caking of built granule.

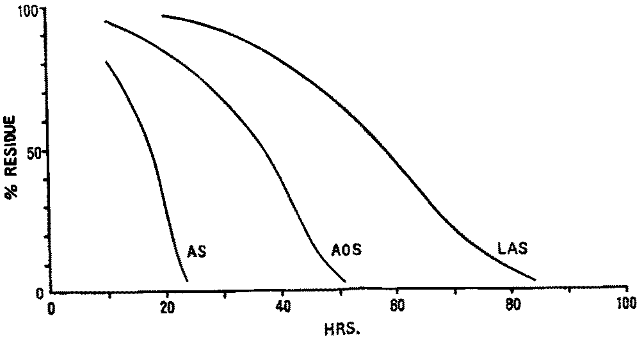

FIG. 13. Rate of biodegradation.

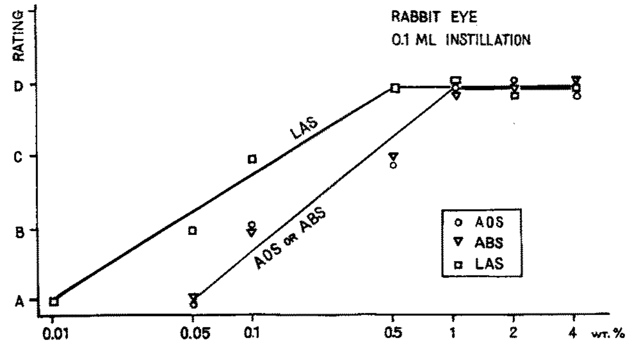

FIG. 14. Eye irritation threshold test.

marized in Table V. Both tests are rated from zero (no reaction) to five (strong reaction) on the two to seven symptoms of erythema, fissuring, papula, vesicle, pityriasis scale, supple and irritation. The hand immersion test proceeds by alternate 1 min hand immersion followed by 1 min hand air drying 30 times. The ordinary procedure is applied for the patch test. Hand immersion shows AOS to be less irritating than ABS; the patch test shows the same level for AOS, ABS, LAS and AS.

Performance Assessment by Housewives

Marketing of our new AOS-based detergent was started in March 1967 and followed by market survey to find the housewives' assessment. The survey was conducted by an independent survey company, and approximately 300 housewives who had purchased and used our new product were interviewed. Their responses coincided well with what we had expected from our test results (Table VI).

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