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(54) Aqueous thixotropic cleaning composition.

(57) Aqueous liquid cleaning compositions incorporate as thickeners a combination of clays of particle size 0.001 to 1 micron and polymeric thickener agents. This combination imparts not only beneficial viscosity to the compositions, but also improves phase stability and reduces loss of chlorine bleach in the aqueous environment. Moreover, the non-phosphate cleaning compositions of the invention have surprisingly effective cleaning performance.

AQUEOUS THIXOTROPIC CLEANING COMPOSITIONS

BACKGROUND OF THE INVENTION

Cleaning compositions for use in automatic dishwashing machines have become quite popular. The market in these products has expanded significantly in the last decade due to more consumers having dishwashing machines in the home as well as to more frequent use of dishwashing machines in order to clean dishes.

Powder dishwashing compositions are recognized to have a very good cleaning performance. However, powders have several aspects which makes their use inconvenient. Thus, powders may spill or sift from the box or pouring spout, creating deposits of powder in undesired places. Also, powders are difficult to dose into dishwashing machines because they pour very quickly into the small dispensing cups of dishwashing machines. Further, the powders are subject to caking when stored over time in conditions of high ambient temperature or humidity.

These undesirable aspects of powders have given rise to automatic dishwashing liquid products. Unlike powders, liquids do not sift or escape from their container unless squeezed through the opening and are not subject to caking. Also, liquids are easier to dose into the dispensing cup for two reasons: automatic dishwashing liquids ("autodish liquids") are viscous and so pour more slowly than powder; and liquids are usually dispensed through a small opening, so a smaller stream of cleaning product is directed toward the dispensing cup. The result is simpler and neater dispensing of the product. Further advantages of liquid autodish liquids are rapid dissolution in the wash liquor and manufacture under simpler processes than powders.

However, autodish liquids themselves are subject to several problems. A major drawback to such liquids is their tendency to undergo phase separation, or syneresis. When this phase separation occurs, the solids suspended in the liquid, such as thickening agents, builder salts or china glaze protection agents, settle from the liquid. The resultant product has a clear or translucent layer and an opaque, moist layer of solids. This phase separation is unattractive to consumers, in that it seems to suggest the product is somehow impaired or defective. Thus, one object of the present invention is to make an autodish liquid with improved phase stability.

There is a further drawback to autodish liquids which are built with non-phosphate materials. In phosphate-built compositions, the builder is present at a level above its solubility and so is in the form of suspended solid. When water-soluble builder material is used, the viscosity of the resulting composition is not retained in automatic dishwashing cups provided for detergent. The rheology of the composition is also quite different from that of conventional phosphate-built liquids. Thus a further object of the present invention is to provide a non-phosphate built composition with rheology and viscosity similar to conventional autodish liquids.

Another drawback to conventional autodish liquids is the loss of bleach activity which occurs during product storage. Autodish liquids are usually aqueous compositions. Chlorine bleach is generally incorporated into these compositions for improved cleaning performance. However, the longer chlorine bleach is stored in an aqueous environment, the more decomposition of bleach occurs, with concomitant loss of bleach activity. Thus, a further object of the present invention is making an autodish liquid composition having reduced chlorine bleach loss.

Conventional autodish liquids are phosphate built, that is they incorporate phosphate compounds to soften the water of the wash liquor in the dishwashing machine, and also to help suspend particulate soils. However, despite the effectiveness of phosphate builders, there are mounting efforts to ban use of phosphate compounds in household cleaning compositions. This has created considerable demand for phosphate-free machine dishwashing compositions. Considerable efforts have been made to identify suitable phosphate builder substitutes, but no fully satisfactory phosphate machine-dishwashing composition has yet been obtained: drawbacks to phosphate substitutes include their poor calcium or magnesium binding power, their poor solids suspension and incompatibility with chlorine bleach. Phosphate builder replacements are usually vulnerable to chlorine bleach degradation. Thus, compositions containing non-phosphate builders not only lose builder, but also substantial amounts of their chlorine bleach. These drawbacks have conventionally resulted in poorer cleaning by compositions which are substantially free of phosphate builder. Thus, yet another object of the present invention is an autodish liquid which is substantially free of phosphate yet has cleaning performance and chemical stability to chlorine bleach which is comparable to phosphate built compositions.

SUMMARY OF THE INVENTION

The compositions of the invention are aqueous liquid cleaning compositions which incorporate as thickeners a combination of certain clays and polymeric thickener agents. This combination is superior to either the clay or polymeric thickener alone in that it imparts not only beneficial viscosity to the compositions, but also improves phase stability and reduces loss of chlorine bleach in the aqueous environment. Moreover, the non-phosphate cleaning compositions of the invention have surprisingly effective cleaning performance.

One embodiment of the invention is an aqueous liquid cleaning composition comprising:

a) 1-5% layered clay having particle size of from about 0.001 to 1.0 micron;
b) 0-5% polymeric thickener;
c) 0.5-40% builder;
d) 0.1-5% available chlorine from bleach; and
e) 5-40% silicate the composition having clay and polymeric thickener present in a weight ratio of from 40:1 to 5:1.

In preferred embodiments of this composition, the clay is a synthetic hectorite and the polymeric thickener is a cross-linked polyacrylate of molecular weight of 500,000 to 5,000,000.

A further embodiment of the invention is an aqueous liquid cleaning composition comprising:

a) 1-5% layered clay having particle size of from about 0.001 to 1.0 micron;
b) 0-5% polymeric thickener;
c) 0.5-40% builder;
d) 0.1-5% available chlorine from bleach; and
e) 5-40% silicate, the composition being substantially free from phosphate and having clay and optionally polymeric thickener which when present should be in a weight ratio of clay to thickener of from 40:1 to 5:1. The composition may be substantially free of other thickening or stabilizing agents, such as multivalent metal ions, long chain fatty acid or mixtures thereof.

In such embodiments, the builder is a polymeric polycarboxylate, although of much smaller size than the polymeric thickener, having molecular weight of 2,000 to 6,000.

The composition is thixotropic and has viscosity of from 1,000 to 500,00 cps at 5 sec^{-1}.

One preferred embodiment of the composition is an automatic dishwashing detergent.

Two further embodiments of the composition may contain colorant and/or opacifying agent; and surfactant, respectively.

In a preferred embodiment, the amount of silicate and clay are present in the composition at a ratio of from 9:1 to 2:1, preferably 7:1 to 2:1 and most preferably 5:1 to 2:1. When the optional polymeric thickener is present, the ratio of silicate to clay may be from 12:1 to 2:1, preferably 10:1 to 2:1 and most preferably from 8:1 to 2:1.

A further aspect of the invention is a method of imparting phase or bleach stability to a chlorine-containing thixotropic cleaning composition. This method comprises incorporating into the composition the stabilizing system of clay and polymeric thickener in particular amounts and in a relative weight ratio to one another.

In another embodiment of the invention, improved cleaning performance is imparted to a non-phosphate cleaning composition by adding the stabilizing system plus the polyacrylic builder described above.

Yet another aspect of the invention is a method of producing the thixotropic aqueous cleaning composition. In one embodiment of the process, the clay is dispersed in water to form a slurry, heated to 40°C and stirred, after which polymeric thickener then silicate are added and stirred. Alternatively, the water may first be heated and clay then added.

In another embodiment, an amount of non-phosphate builder is added to the water prior to the clay to impart better viscosity to the composition during handling.

DETAILED DESCRIPTION OF THE INVENTION

A first embodiment of the invention is a cleaning composition comprising

a) 0.1 to 5% of a layered clay having particle size of from about 0.001 to 1.0 micron;
b) 0 to 5% of a polymeric thickener;
c) 0.5 to 40% builder;
d) 0.1 to 10% available chlorine from bleach; and
e) 5 to 40% silicate, the layered clay and optionally a polymeric thickener being present in a weight ratio

of from 40:1 to 5:1.

The clay and polymeric thickener of the composition together constitute a stabilizing system. When they are both present in a certain relative weight ratio to one another, the clay and polymeric thickener impart not only improved product stability but also reduced loss of the bleach in the aqueous environment.

The size of the clay particles renders them suitable for use in the present compositions. Thus, the very fine synthetic hectorite clays are especially preferred because their small particle is found to be especially useful in imparting the desired properties to the compositions thickened and stabilized with the two-component stabilizing system. It should be understood that "particle size" is understood to mean the size of the discrete grains of dry clay after they have been moistened. A suitable particle size for the clays of the invention is from 0.001 to 1.0 micron, more preferably from 0.005 to 0.5 micron, and most preferably from 0.01 to 0.1 micron. If the clay materials mentioned below have particle size larger than desired, the materials may be subjected to grinding or crushing in order to help bring the average size of the particles within the desired size range.

Suitable clays for the thickening system and the cleaning compositions may include organophilic and layered clay minerals belonging to the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are: 1) smectites, e.g. montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite; 2) illites, e.g., bravaisite, muscovite, paragonite, phlogopite; 3) chlorites, e.g., corrensite, penninite, donbassite, sudoite; 4) attapulgites, e.g., sepiolite, and polygorskyte.

The layered clay minerals may be either naturally occurring or synthetic. Preferred clay minerals for use in the present invention are natural or synthetic smectites and attapulgites, (particularly the hectorites, montmorillonites and bentonites,) and of these the hectorites are especially preferred. Many of the above clays are available commercially, and typical examples of commercial hectorites are the Laponites ex Laporte Industries Ltd. , England; Veegum Pro and Veegum F ex R. T. Vanderbilt, USA; and the Barasyms, Macaloids and Propaloids ex Baroid Division, National Lead Company, USA.

Particularly preferred commercial hectorites are the synthetic hectorites Laponite S, Laponite XLS, Laponite RD and Laponite RDS, of which Laponite XLS is especially preferred. This is a synthetic hectorite having the following characteristics: analysis (dry basis) SiO2 59.8%, MgO 27.2%, Na2O 4.4%, Li2O 0.8%, structural H2O 7.8%, with the addition of tetrasodium pyrophosphate (6%); specific gravity 3.54; and bulk density 1.0.

The effective level of the layered clay in the compositions having the stabilizing system is from about 1% to about 5% by weight, preferably from about 2.0% to about 4.5% by weight, and most preferably from about 2.5% to about 3.5% by weight.

The polymeric thickener of the stabilizing system may suitably be a polycarboxylic polymer that has been inter-polymerized with a multi-vinyl or multi-allylic functionalized cross-linking agent. Preferably, the polycarboxylic polymer is interpolymerized with a polyalkenyl polyether of a polyhydric compound. The polyhydric compound should have at least 4 carbons and 3 hydroxy groups. These thickeners are described in U. S. Patent 2,798,053, in U.S. patent 4,130,501 and in our copending application by Elliott et al. , Serial No. 202,087, filed on June 2, 1988. All of these references are hereby incorporated by reference. More specifically, the thickeners are water-dispersible copolymers of an alpha-beta monoolefinically unsaturated lower aliphatic carboxylic acid cross-linked with a polyether of a polyol. The polyol may be selected from the group consisting of oligosaccharides, reduced derivatives thereof in which the carbony; group is converted to an alcohol group, and pentaerythritol. The hydroxy grops of said polyol are etherified with allyl groups, said polyol having at least two allyl groups per polyol molecule. A suitable copolymer is one of acrylic acid with low percentages (0.71 to 1.5%) poly allyl sucrose.

Molecular weights of the cross-linked polymeric thickener may range from about 400,000 up to 10,000,000, preferably between 500,000 and 5,000,000, most preferably from about 1,000,000 to 4,000,000. Examples of commercially available cross-linked polymers based upon allyl sucrose modified polyacrylic acid are the Carbopol resins manufactured by the B. F. Goodrich Chemical Company. These materials include Carbopol 941R (m.w. 1,250,000), Carbopol 934R (m. w. 3,000,000) and Carbopol 940R (m.w. 4,000,000). Carbopol 950 R, Carbopol 951 R and Carbopol 954 R. Most preferred is Carbopol 934R .

The polymeric thickener of this invention may be present in an amount from about 0 to about 5% by weight, preferably from about 0.1 to about 1% by weight, and most preferably from about 0.15 to about 0.4% by weight of the composition.

In the stabilizing system, when the layered clay and polymeric thickener are both present, they should be present in a relative weight ratio of from about 40:1 to about 5:1, preferably 35:1 to 10:1, and most preferably from about 30:1 to 15:1.

It should be noted that further elements necessary to thicken other systems incorporating a clay and a polymer need not be present in the stabilizing system here. Thus, the instant clay and polymer system does not require the presence of a multivalent ion, a long chain fatty acid or a combination thereof in order to thicken compositions. It is believed that no other element is necessary here to thicken. In fact the cleaning composition incorporating the stabilizing system may, when formulated, be substantially free of multivalent ions or long chain fatty acids or a conbination thereof or other thickening agents except the layered clay and cross-linked polymeric thickener.

The cleaning composition includes a builder element in order to sequester hardness ions, ie calcium and magnesium which are present in the wash water. If these cations are not sequestered, they can form undesirable precipitates with soil and surfactant molecules. These precipitates can remain on the surfaces to be cleaned and cause spotting or filming.

The builder element of the composition may be a phosphate-containing compound. These compounds include salts of orthophosphates, pyrophosphates and polyphosphates, as well as organophosphates. Suitable counterions include alkali metal ions, and ammonium or substituted ammonium. The preferred phosphate builders are polyphosphate salts, because these have the greatest solubility and hardness ion sequestering effect. Most preferred are hydrated alkali metal salts of polyphosphate. These hydrated salts form needle-like crystals, as opposed to the cubic crystals formed by unhydrated phosphates. These needle-like crystals are less likely to coalesce into larger crystals. When the non-hydrated phosphate salt crystals do coalesce, they cause a rise in viscosity of the liquid over time. Rather than have this uncontrolled increase in viscosity, it is preferred to avoid such a rise in viscosity by using hydrated phosphate salts at the outset.

The cleaning composition may further or alternatively comprise a non-phosphate builder. Such builders may suitably be inorganic, such as alkali metal carbonates such as are well known. Alternatively, the builder material may be organic, such as alkali metal salts of citric acid or other polycarboxylic compounds. It is found that polymeric polycarboxylic molecules of molecular weight of from about 1,000 to 100,000 are most preferred as non-phosphate builders, especially those having bleach stability, with molecular weights of 2,000 to 20,000 being preferred and 3,000 to 10,000 being most preferred. Suitable polycarboxylic polymeric compounds include homopolymers of acrylic acid, maleic acid, itaconic acid and the like, as well as copolymers of such monomeric materials. Commercially available non-phosphate builder materials include Alcosperse 602N ex Alco Chemical Company (MW 4,500 having 45% solids); and Sokalan PA-30 (MW 8,000).

The builder compounds are present in the composition at from about 0.1 to about 4.0%, preferably from 0. 5 to 20% and most preferably from 2 to about 10%.

If the amount of polymeric polycarboxylate builder required to sequester hardness cations present in water were stoichiometrically related to the amount of hardness cations, then a hardness level of 240 ppm would require about 20% of polymeric builder; builder levels of 0.5 to 20% or 2 to 10% would run the risk of being substantially underbuilt. However, it is found that even at low levels, the polymeric polycarboxylate provides sufficient building activity to sequester hardness ions and provide acceptable cleaning. Without in any way limiting the invention herein described, applicants believe this level of building from low levels of builder is due to the "threshold effect."This colloidal chemical effect, hardness ions precipitating in the presence of certain polymers form flawed crystals. These crystals do not grow to the extent they would in the absence of polymer. Thus, these flawed crystals remain dispersed; moreover, these crystals do not have the same propensity to adhere to surfaces, and so are not able to cause filming and spotting on glass and other surfaces.

When the cleaning composition is used as an automatic dishwashing formulation, it will normally also contain an oxidizing agent. Traditionally, liquid dishwashing compositions have for this purpose used sodium hypochlorite because it is inexpensive. Other oxidizing agents may however be used. For instance, it is also possible to use heterocyclic N-bromo and N-chloro imides such as trichlorocyanuric, tribromocyanuric, dibromo and dichlorocyanuric acids, and salts thereof with water solubilizing cations such as potassium and sodium. An example of a hydrated dichlorocyanurate acid is Clearon CDB 56, a product manufactured by the Olin Corporation. The oxidizing material will be present in the composition such that from about 0.1 to 1.5% available chlorine is produced. Preferred compositions will have 0.5 to 1.2% available chlorine.

Automatic dishwashing detergent compositions based upon this invention will also contain alkali metal silicate.

This material is employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor, and protector of glaze on china tableware. Especially effective is sodium silicate having a ratio of $SiO_2:Na_2O$ from about 1.0 to about 3.3, preferably from about 2 to about 3.2. The silicate may be used in the form of an aqueous liquor or a solid. It will be present from about 1 to 50 % by weight, more preferably from about

5 to about 20% by weight of the composition.

Amounts of water present in the liquid compositions should neither be so high as to produce unduly low viscosity and fluidity, nor so low as to produce unduly high viscosity and low flowability, thixotropic properties in either case being diminished or destroyed. Water will therefore generally be present in an amount ranging from about 25 to 80%, preferably from about 45 to 75%, and most preferably from about 55 to 65% by weight of the composition.

One or more bleach-stable surfactants may optionally be incorporated in the cleaning compositions. These surfactants should be of the low-foaming type, since foam interferes with the dishwasher cleaning action. Suitable low foaming anionic surfactants may be very useful for the cleaning compositions, especially when combined with effective defoaming materials. Anionics are desirable because they are more stable toward hypochlorite than many nonionic surfactants. Among the suitable anionic surfactants are alkyl diphenyloxide sulfonate, alkyl naphthalene sulfonate, sodium 2-acetamidohexadecane sulfonate and nonionic alkoxylates having a sodium alkylene carboxylate moiety linked to a terminal hydroxy group of the nonionic through an ether bond. Suitable nonionics, which have bleach stability, are those described in our copending U.S. patent application by Gabriel et al. , Serial No. 183,512, filed April 14, 1988, which is hereby incorporated by reference.

When present, surfactants are employed at an amount from about 0.1 to about 10%, preferably from about 0.15 to 5%, and most preferably from about 0.2 to 3% by weight of the composition.

Defoaming of the wash may be accomplished by the presence of any of number of commercially available defoaming agents. These agents may be of the general type of slightly soluble alkyl carboxylates, alkyl phosphates, hydrocarbon waxes, hydrophobic silicas, silicone defoamers or many others. In addition to being an effective defoamer, the preferred species are stable to hypochlorite. Because some defoaming agents tend to deposit on glassware washed with the instant composition, thereby causing unsightly filming, preferred defoaming agents are those which do not deposit on glassware. The defoamer will optionally be present in the composition from about 0.05 to 5%, preferably from about 0.1 to 1%, and most preferably from about 0.1 to 0.5% by weight of the composition.

Minor amounts of other various adjuvants may be present in the cleaning composition. Thus, the composition may further include perfumes, colorants, opacifying agents (e.g. titanium dioxide), flow control agents, soil suspending agents, alkaline agents, antiredeposition agents, anti-tarnish agents, enzymes and other functional additives. When present, opacifying agents may be used at levels of 0.05-05%.

When non-phosphate builder elements are employed in the cleaning composition described herein, the composition is found to have surprisingly good cleaning performance. Glass appearance is usually an indication of cleaning performance. Cleaning by phosphate built compositions is usually superior to that by non-phosphate compositions. This is because phosphate is such an effective hardness ion sequestrant and soil suspending agent. Surprisingly, the compositions described herein having non-phosphate builder impart an improved glass appearance to washed glasses. This improved glass appearance can be equal to that of phosphate-built compositions. Even at high levels of water hardness, where calcium and magnesium are likely to cause filming and spotting precipitates, the non-phosphate built compositions are found to have spotting and filming at an acceptably low level.

The non-phosphate compositions described herein also have robust cleaning performance with respect to difficult soils. Thus, these compositions are found to remove egg yolk and dried cereal as effectively or better than phosphate-built compositions. This parity performance is surprising in that non-phosphate cleaning compositions conventionally do not clean as well as phosphate-built ones.

Although the embodiments described above have been specifically directed toward automatic dishwashing compositions and the foregoing specification has detailed such formulated products, it must be emphasized that the base cleaning composition may be utilized for other purposes. Thus, it is envisioned that the cleaning composition of this invention may be useful in products such as fabric washing formulations, hand dishwashing liquids, toilet bowl scrubs, pot/pan cleaners, fabric softeners, and denture cleaners.

The cleaning composition may be made by mixing the components in water in any order. Thus, for example, the clay and polymeric mixer may be mixed in dry form then added to water and stirred for 10 to 15 minutes. This stirring disperses the clay and thickener and allows the clay to swell and the polymeric thickener to be hydrated. Stirring is preferably performed at high speeds on conventional mixing equipment. Next, alkaline salts of the composition are added to the aqueous mixture. These are stirred until dissolved, usually for about 10 minutes. Then the builder is added and stirred until dispersed. Polymeric builder is usually in liquid form and so requires short mixing time. Finally, the aqueous mixture is allowed to cool to about room temperature, and the bleach component is added and stirred.

However, applicants have discovered that certain advantages may be obtained when specific orders of addition are employed.

Thus, the invention further comprises a method of producing the thixotropic aqueous cleaning composition, the method comprising:

a) clay is dispersed in water at or below room temperature to form an aqueous clay slurry;
b) the aqueous clay slurry is heated to 40 °C and stirred for about 40 minutes;
c) polymeric thickener is then added and stirred in for up to 30 minutes;
d) silicate is added and stirred in for 20 minutes;
e) the aqueous slurry is cooled to below 30 °C;
f) bleach is added with mixing. Alternatively, the water may be heated to 40 °C and the clay then dispersed therein to form a slurry which is stirred for 30-60 minutes.

When either order of steps is followed, the resulting composition has good phase stability. It is noted however, that regardless of the order of addition used, there is an increase in the viscosity of the slurry when the clay is added. Thus, the viscosity increases observed are in proportion to the amount of clay or the type of clay added. These viscosity increases may render processing more difficult.

Applicants have further discovered that this change in viscosity can be largely obviated by a slight change in the order of addition. Thus, where an amount of the non-phosphate builder is added to the water in the vessel prior to the clay, viscosity increases which can increase production times are avoided. The amount of builder which is added is up to 10% of the weight of the clay present in the final composition.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLES

EXAMPLE 1

A liquid autodish composition is made according to the following formulation

Sodium tripolyphosphate	8.5%
Potassium tripolyphosphate	5.4%
Sodium metasilicate	21.0%
Sodium hypochlorite (aq) (as av Cl_2)	1.3%
Laponite XLS clay	3.5%
Carbopol 934 polyacrylate	0.2%
Water	balance

The water is added to a glass beaker placed in a 40 °C water bath. The Laponite clay and Carbopol are mixed together and then added to the water over 1 minute. Mixing in the water is provided by a Talboy stirrer fitted with a propellor-type agitator. The mixture is stirred for a few minutes to hydrate and swell the thickeners. The metasilicate is then added over 5 minutes, after which the mixture is stirred for another 5 minutes. The sodium tripolyphosphate and potassium tripolyphosphate over are then added over 10 minutes. The complete mixture is then stirred for a further 10 minutes to dissolve most of the phosphates.

The mixture is then cooled to 30 °C with a 20 °C water bath, and the hypochlorite solution is then added slowly. The resulting autodish liquid is a thick, pasty, opaque liquid which flows slowly.

EXAMPLE 2

An important consideration in formulating an autodish liquid is its retention in the dispensing cup of the machine dishwasher. The viscosity of the autodish liquid must be high enough to retain the liquid in the cup during a series of pre-washes and rinses.

The following two formulations are made and dispensed into the dispensing cups of two different dishwashing machines: the Sears Kenmore and the Bosch S 512 Economic models.

Clay/Polymer thickened composition		Commercial Autodish liquid	
Laponite XLS	3.5 %	Sodium tripolyphosphate	16%
Carbopol 934	0.2	Sodium carbonate	6
Sodium metasilicate	5.0	Sodium silicate	15
Sodium silicate	15.0	Sodium hydroxide	1.4
Hypochlorite solution (final level of available chlorine is 1.2%)	9.0	Aluminum stearate	0.1
Water	Balance	Bentonite clay	3.0
		Monoalkyl acidphosphate	0.1
		Available chlorine from bleach	1.0
		Water	Balance

After 2 pre-washes, the volume of dishwashing fluid remaining in the cup of each machine is measured. The results are as follows:

	% Volume retained	
Commercial autodish liquid	70% (Kenmore)	100% (Bosch)
Clay/Polymer autodish liquid	80% (Kenmore)	100% (Bosch)

Thus, the cleaning composition having the stabilizing system has cup retention as good as a commercially available product.

EXAMPLE 3

The compositions from Example 2 are prepared, however further incorporating into the composition having the stabilizing system a non-phosphate builder: ie, 4.5% by weight of Alcosperse 602N, a sodium salt of polyacrylic acid having average molecular weight of from 4,500. A sample of both autodish liquids is stored at room temperature, 40° C and 50° C. The samples are stored at these temperatures for sixteen weeks, at which time the volume in each sample which has undergone syneresis is measured. As shown in Fig. 1, the percentage of syneresis is as follows:

	RT	40° C	50° C
Nonphosphate autodish liquid	12%	4%	6%
Commercial autodish liquid	16%	28%	32%

Thus, the physical stability of the composition containing the layered clay/polymeric thickener stabilizing system is superior to that of the commercial clay-thickened autodish liquid.

EXAMPLE 4

The non-phosphate composition made in Example 3 is made holding the amount of Carbopol 934 constant at 0.2% by weight while varying the amount of Laponite XLS from 0 to 4% by weight of tho composition, in 1.0% increments. The viscosity of each composition is measured using a Haake viscometer at 5 sec $^{-1}$ and 21 sec $^{-1}$. The viscosity measurements are shown in Fig. 2.

Similarly, the non-phosphate composition made in Example 3 is made holding the amount of Laponite XLS constant at 3.5% while varying the amount of Carbopol 934 from 0 to 0.4% by weight. Viscosity is again measured at 5 and 21 sec $^{-1}$; these viscosity measurements are illustrated in Fig. 3.

The desirable viscosity range for autodish liquids extends from 3 to 8 Pa S at 5 sec $^{-1}$. Thus, Fig. 3 shows the useful range of Carbopol 934 is from 1.5 to 3.5% by weight of the composition.

EXAMPLE 5

To test hypochlorite stability, a batch of the commercial autodish liquid from Example 2 and of the nonphosphate autodish liquid composition of claim 3 (4.5% Alcosperse 602N and 1% available chlorine) are formulated. A sample of each is stored at three different temperatures: room temperature, 40° C and 50° C. Each week, 15 ml samples are drawn from each 500 ml sample and tested by standard iodometric titration for % available chlorine. The results of this test are illustrated in Figs. 4 and 5. After sixteen weeks at room temperature, the non-phosphate composition (Fig. 4) has about 70% of its chlorine. Less is retained at the higher temperatures.

In the commercial formulation chlorine loss at room temperature (Fig. 5) is about equal to that for the non-phosphate composition. However, it is clear the non-phosphate composition delays chlorine loss at the elevated storage temperatures. Thus, for example, the commercial formulation is found to have no chlorine remaining after twelve weeks, while the composition having the clay/polymer stabilizing system does not reach this level until fifteen weeks. This shows the composition with the clay/polymer stabilizing system has active chlorine for nearly one month longer than the commercial formulation. Further comparison of the rates of loss of available chlorine shows a steeper loss in the commercial composition in the first four weeks of the test.

EXAMPLE 6

In order to evaluate the cleaning performance of the non-phosphate built cleaning compositions, the appearance of glasses washed with the non-phosphate compositions is compared to that of glasses washed with a commercial phosphate built compositions.

Glass appearance tests are run in Bosch S-512 Economic dishwashers at 140° F and 120 ppm water hardness. The non-phosphate and commercial dishwashing compositions are those listed in Example 3 and 2 above, respectively.

In the test, two washing machines are loaded with ten clear glass plates and drinking glasses (all of which are clean and spotless). Forty grams of a fatty soil are then smeared on the interior of each washing machine door. The soil consists of four pounds of Imperial margarine and four packets (12.8 ounces each) of Carnation non-fat dry milk mixed together until smooth. Forty grams of the cleaning composition of either Example 3 or 2 is then loaded into the washing machine cup dispenser. The glassware is then subjected to a short wash cycle. After the wash cycle, each plate and glass is removed from the washer and evaluated for spotting and filming according to the following scale:

Spotting Scale	Filming Scale
0 = spotless	0 = no film
1 = few spots	1 = trace of film
2 = 1/3 glass spotted	2 = slight film
3 = 2/3 glass spotted	3 = moderate film
4 = glass completely covered with spots	4 = heavy film
	5 = chalky coating on glass

After evaluating the glassware, the glasses and plates washed in the first machine are returned to the second machine and those from the second are returned to the first machine. Soil and detergent are again put in the machine and another cycle is run. Four wash and evaluation cycles are run, the glassware being switched from one machine to the other after each wash cycle to remove any machine effect. The summary of the spotting and filming evaluation results appear in Figures 6 and 7. As the graphs of Figures 6 and 7 illustrate, the non-phosphate composition not only has filming and spotting scores comparable to those of the commercial phosphate-built composition, but scores that are slightly superior to the commercial composition scores.

EXAMPLE 7

The clay/polymeric thickener autodish liquid of Example 2 above is made and tested for relative cleaning performance against the following autodish liquid formulation:

Sodium tripolyphosphate	24.5%
Sodium disilicate (2.0 ratio)	23
Sodium hydroxide	2.0
Sodium alkyl sulfonate (alkyl = C10-C20)	0.1
Alkyl phosphate (alkyl = C10-C20)	0.2
Available chlorine from hypochlorite	1.2
Water	Balance

Each formulation is used to clean two different types of soil: a "cream of wheat" hot breakfast cereal soil and an egg yolk soil. The soils are prepared as follows. In a one quart saucepan, 300 ml of distilled water and 0. 7 g of sodium chloride are brought to a boil. The heat is lowered and 24 g of cream of wheat are added. The cereal is cooked over low heat for 10 minutes with stirring then cooled to room temperature. 200 g of the cooked cereal is then blended with 100 ml of distilled water in an OsterizerR blender for 2 minutes. The resulting mixture is strained through a 32 mesh screen. Egg yolk soil is prepared by separating yolks from 10 large raw eggs, and blending 200 ml of yolk and 45 ml of distilled water for 3 minutes in an OsterizerR blender.

A thin layer of one of the soils (about 0.5 g) is applied to clean dishes with a Black & Decker paint sprayer. The dish is allowed to dry for 10 to 15 minutes, and a second layer of the same soil is applied. Dishes soiled with cream of wheat are dried overnight; dishes soiled with egg yolk are baked in an oven preheated to 100° C for 50 minutes, then aged overnight.

The soiled dishes are placed randomly in a Bosch S 512 Economic model dishwasher. Either the autodish liquid from Example 2 or the one shown above is used to clean the dishes in a normal wash cycle. Dishes soiled with cream of wheat are scored for soil removal by dipping in a 1:10 aqueous solution of iodine and evaluating the amount of soil remaining. Dishes soiled with egg yolk are evaluated as is. Both are scored on a scale of 0 to 5, with 0 being no soil removal and 5 corresponding to complete soil removal. Results appear in Fig. 8 and indicate that even though the formulation from Example 2 is a non-phosphate formulation, it has a cleaning performance comparable to phosphate-built formulations.

In a preferred embodiment of the cleaning composition, no polymeric thickener is present, the level of silicate is at least 10% and silicate and clay are present in the composition at a ratio of from 7:1 to 2:1, preferably 5:1 to 2:1 and most preferably 4:1 to 2:1. Silicate at these levels with the clay imparts viscosity and. phase stability to the composition. Above the 7:1 ratio however, silicate (in the absence of polymeric thickener) does not always impart phase stability.

When polymeric thickener is present, the ratio of silicate to clay may be above 7:1, i.e. from 12:1 to 2:1, preferably 10:1 to 2:1 and most preferably from 8:1 to 2:1. When the amounts of silicate and clay are within these higher ratios, the physical stability of the resulting composition is improved, as demonstrated in the following Examples.

EXAMPLE 8

The Sample is made with the formula listed below:

Component	Wt.% Active
Deionized Water	73.65
Laponite XLS	3.50
Carbopol 934	0.20
Sodium Metasilicate	5.00
Britesil H 20 (Sodium disilicate, SiO_2:NaO_2 = 2.0)	12.15
Alcosperse 602 N	4.50
Sodium Hypochlorite (as Available Chlorine)	1.00
	100.00

The sample is prepared on a 1000 g batch scale using a 1 L beaker and a mechanical stirrer fitted with a variable speed control and a simple turbine style blade with about a 1.5 inch radius.

The Laponite clay is sifted into the water with sufficient agitation to provide moderate vortexing. The clay is allowed to disperse initially in water at or somewhat below room temperature but then the aqueous clay slurry is heated up to about 40 °C. Stirring is continued at this temperature for about 40 minutes. Laponite XLS slurries are relatively low viscosity homogeneous liquids and appear to be free of lumps. The beaker is then allowed to cool to room temperature during the remaining addition steps. The speed of agitation is increased and the Carbopol polymer is sifted in as a free flowing powder. About 30 minutes is allowed for dispersion and swelling of the polymer. The addition of sodium metasilicate follows and is observed to cause an increase in viscosity initially and then with continued addition, a partial decrease in viscosity. Addition of Britesil H 20 is next; this component causes some increase in viscosity during the dissolution of the granulates and is best achieved by an increase in the speed of the turbine blade. Alcosperse 602N is then added as the neutralized 40 to 45 wt. % solids solution. Little change in viscosity is noted. The batch is cooled and sodium hypochlorite is added. The maximum batch temperature for addition of the bleach is 30 °C.

The physical stability of the resulting formulation was found to be excellent over 6 weeks at 40 °C.

EXAMPLE 9

Nineteen samples of autodish liquid are made based on the formulation appearing in Example 8 in which however the amounts of clay, silicate and polymeric thickener are varied as shown in Table 1 below.

The physical stability and the viscosity of the nineteen samples are measured at a lower and higher shear rates (5 s^{-1} and 21 s^{-1}). Physical stability is measured as a function of volume % separation after 4 weeks of storage at room temperature. Viscosity is measured using a Haake Rotovisco RV100 coupled with a M150 test unit. The measurement is performed using the shear rate sweep mode at a rate of 0. 25 s^{-2}.

The results of these investigations are summarized in Table 1.

Table 1. Viscosity and Physical Stability of ADL Samples

Sample	Laponite XLS Wt.%	Britesil H 20$^+$ Wt.%	Carbopol 934 Wt.%	5 s^{-1*}	21 s^{-1*}	Physical Separation Vol.%**
1	3.50	25.0	0	11.3	2.4	21.1
2	3.50	25.0	0.4	15.3	3.0	2.4
3	3.50	21.5	0.2	10.0	3.6	0
4	3.50	18.0	0	9.6	2.0	0
5	3.50	18.0	0.4	8.9	1.8	0
6	2.38	25.0	0.2	5.3	1.2	0
7	2.38	25.0	0.2	4.0	1.0	20.7
8	2.38	21.5	0	4.8	1.2	0
9	2.38	21.5	0.2	4.9	1.1	1.7
10	2.38	21.5	0.2	4.3	1.0	3.4
11	2.38	21.5	0.2	4.6	1.0	0
12	2.38	21.5	0.2	3.8	0.9	3.1
13	2.38	21.5	0.4	4.5	1.2	1.6
14	2.38	18.0	0.2	3.2	0.7	3.3

15	1.25	25.0	0	2.3	0.8	15.4
16	1.25	25.0	0.4	1.0	0.8	31.4
17	1.25	21.5	0.2	0.8	0.3	36.5
18	1.25	18.0	0	0.8	0.2	17.4
19	1.25	18.0	0.4	0.6	0.3	24.3

+ Expressed as content of an 81% actives solid

* Values expressed as Pa s.

** As absolute normalized percentage of volume.

It is seen from samples 1, 4, 8, 15, and 18 that in the absence of polymeric thickener, the highest ratio of silicate to clay shown to impart phase stability to the composition is 9:1; ratios above 9:1 do not impart phase stability unless at least some polymeric thickener is present (see samples 2, 3, 5, 6, 7, 9, 10, 11-14, 16, 17, and 19). When polymeric thickener is present even at low levels, the ratio of silicate to clay may substantially exceed 9:1 and the formulation remains phase stable.

EXAMPLE 10

The effect of the silicate:clay ratio and of polymeric thickener can also be seen when centrifugation is used as the force which separates the liquid. Samples are prepared as described in Example 9 above which contain 1.75% Laponite XLS, and varied amounts of silicate and polymeric thickener, all other factors (except water) being the same. Samples 1 through 6 are centrifuged for 20 minutes at 1000 RPM (about 325 x G) using a Savant High Speed Centrifuge. Samples 7 through 10 are centrifuged at 2,000 RPM (about 700 G). The volume percent separation of supernatant is an average of two samples measured; results appear in Table 2.

Table 2. Volume Percent Separation as a Function of Silicate and Polymeric Thickener Level

Sample	Silicate Wt.%	Polymeric Thickener Wt.%	Silicate: Clay Ratio	Volume% Separation
1	15	0	8.6	0
2	17	0	9.7	1.6
3	19	0	10.9	8.1
4	21	0	12.0	12.5
5	23	0	13.1	42.6

6	25	0	14.3	60.6
7	25	0	"	64.3
8	25	0.05	"	53.8
9	25	0.10	"	25.8
10	25	0.20	"	4.4

Table 2 demonstrates that raising silicate levels above a ratio of 9:1 substantially increases physical instability of the formulations with great physical instability resulting at ratios in excess of 12:1. However, in the presence of 0.2% polymeric thickener, a silicate:clay ratio of as high as 14.2 is tolerated without significant physical separation.

The invention further comprises a method of producing the thixotropic aqueous cleaning composition, the method comprising:

a) dispersing clay in water at or below room temperature to form an aqueous clay slurry;
b) heating the aqueous clay slurry to 40° C and stirring for about 40 minutes;
c) adding a polymeric thickener to the aqueous clay slurry and stirring for up to 30 minutes;
d) adding a silicate and stirring;
e) the aqueous slurry is cooled to room temperature;
f) bleach is added with mixing.

When this order of steps is followed, the resulting composition has good phase stability. It is noted however, that there may be a large increase in the viscosity of the slurry being mixed when the silicate is added. Such increases in viscosity can retard production rates of cleaning compositions of the invention; any method of avoiding such slow downs would therefore result in higher production rates.

Applicants have further discovered that this change in viscosity can be largely obviated by a slight change in the order of addition. Thus, where some non-phosphate, low molecular weight polycarboxylic acid or salt builder is added to the water in the vessel prior to the clay, viscosity increases which can increase production times are avoided. The amount of builder which is added may be up to 10% of the weight of the clay present in the final composition.

It shall be noted when all or a large portion of the low molecular weight builder is added prior to the clay, the resulting compositions are often found to have poor stability. Thus, applicants further discovered that only a fraction of the low molecular weight polymeric polycarboxylic acid or its salt material ought to be added prior to the clay; the remainder is added at the point indicated above. As shown in Example 12, the amount of this builder to be added prior to clay is up to about 10 % of the total clay weight percent in the composition.

EXAMPLE 11

Increases in viscosity during production of the cleaning composition may be minimized by altering the order of mixing to put some of the low molecular weight polymeric builder into the batch prior to addition of Laponite RD. The following order of addition is followed in making a 1000 g sample.

Component	Wt.% Active
Deionized Water	73.85
Alcosperse 602N	0.15
Laponite RD	3.50
Carbopol 934	0
Sodium Metasilicate	5.00
Britesil H 20	12.15
Alcosperse 602 N	4.35
Hypochlorite (as Available Chlorine)	1.00
	100.00

The batch is prepared as described in Example 10 above except a fraction of the total of the Alcosperse polymer is added to the water prior to the Laponite clay. This amount is 0. 15% of the total composition. This order of addition has the effect of lowering the viscosity of the clay slurry during processing.

Table 4 below contains measurements of the viscosity of the Laponite slurry at various levels of polymer addition prior to the clay. Viscosity is measured at 0.9 sec^{-1} and 20 sec^{-1}. The Quality of the clay dispersion is reflected in the final column: a "+"sign indicates a good quality dispersion having a high final batch viscosity; a"-" sign indicates a partly flocculated dispersion leading to a thin batch with less than acceptable final viscosity and which tends to rapidly physically separate.

Table 3.

The Influence of Polymer on In-process Viscosity Reduction				
Level of Sodium Polyacrylate *		Viscosity		Quality of clay Dispersion
As Wt.% of Laponite RD**	As Actual Wt.% Polymer added before Clay	0.9s^{-1} (Pa•s)	20s^{-1} (Pa•s)	
0	0	184.0	8.2	+
2.3	0.08	64.0	3.7	+
5.0	0.18	0.8	0.4	+
9.2	0.32	7.4	0.8	+
25.7	0.90	30.0	2.0	-
51.4	1.80	10.0	1.0	-
77.1	2.70	4.5	0.3	-
102.9	3.60	0.5	0.1	-
128.6	4.50	0.5	0.1	-

* As solids delivered from Alcosperse 602N prior to addition of Laponite RD

** As weight % of Laponite in a 5.8 wt% slurry which delivers 3.5 wt% Laponite in final formula

These data indicate that the optimal range of low molecular weight polyacrylate to be added prior to the Laponite RD is up to abut 10wt% of the Laponite RD present in the slurry.

Claims

1. A thixotropic aqueous liquid cleaning composition comprising:
(a) 1 to 5% layered clay having particle size of from about 0.001 to 1 micron;
(b) 0 to 5% polymeric thickener;

(c) 0.5 to 40% builder;
(d) 0.1 to 5% available chlorine from bleach; and
(e) 5 to 40% silicate;
where the layered clay and polymeric thickener, when present, are present in relative weight ratio of from 40:1 to 5:1.

2. A cleaning composition as claimed in claim 1 comprising: (a) 2.5-3.5% clay; (b) 0.1-0.3% polymeric thickener; (c) 1-25% sodium polyacrylate having molecular weight of from 3,000 to 6,000; (d) 0.3-2% available chlorine from bleach; and (e) 15-25% silicate.

3. A cleaning composition as claimed in claim 1 or claim 2 where the layered clay is synthetic hectorite.

4. A cleaning composition as claimed in any one of claims 1 to 3 where the polymeric thickener is cross-linked polyacrylic acid or its salt, and has molecular weight of from 500,000 to 5,000,000.

5. A cleaning composition as claimed in any one of the preceding claims where the ratio of clay to polymeric thickener is from 20:1 to 10:1.

6. A thixotropic aqueous liquid cleaning composition comprising:
(a) about 1 to 5% layered clay having particle size of from about 0.001 to 1 micron;
(b) 5 to 40% silicate;
(c) 0.5 to 40% builder; and
(d) 0.1 to 5% available chlorine from bleach;
where the composition is substantially free from polymeric thickening agents and the silicate and clay are present in relative weight ratio of from 7:1 to 2:1.

7. The cleaning composition according to claim 6 wherein the ratio of silicate to clay is from 9:1 to 2:1.

8. A cleaning composition according to any one of the preceding claims where the composition is substantially free from phosphate.

9. A cleaning composition according to any one of the preceding claims where the builder is a sodium salt of polyacrylic acid having average molecular weight of from 1,000 to 10 000.

10. A cleaning composition according to any one of the preceding claims further comprising from 1 to 10% bleach-stable surfactant.

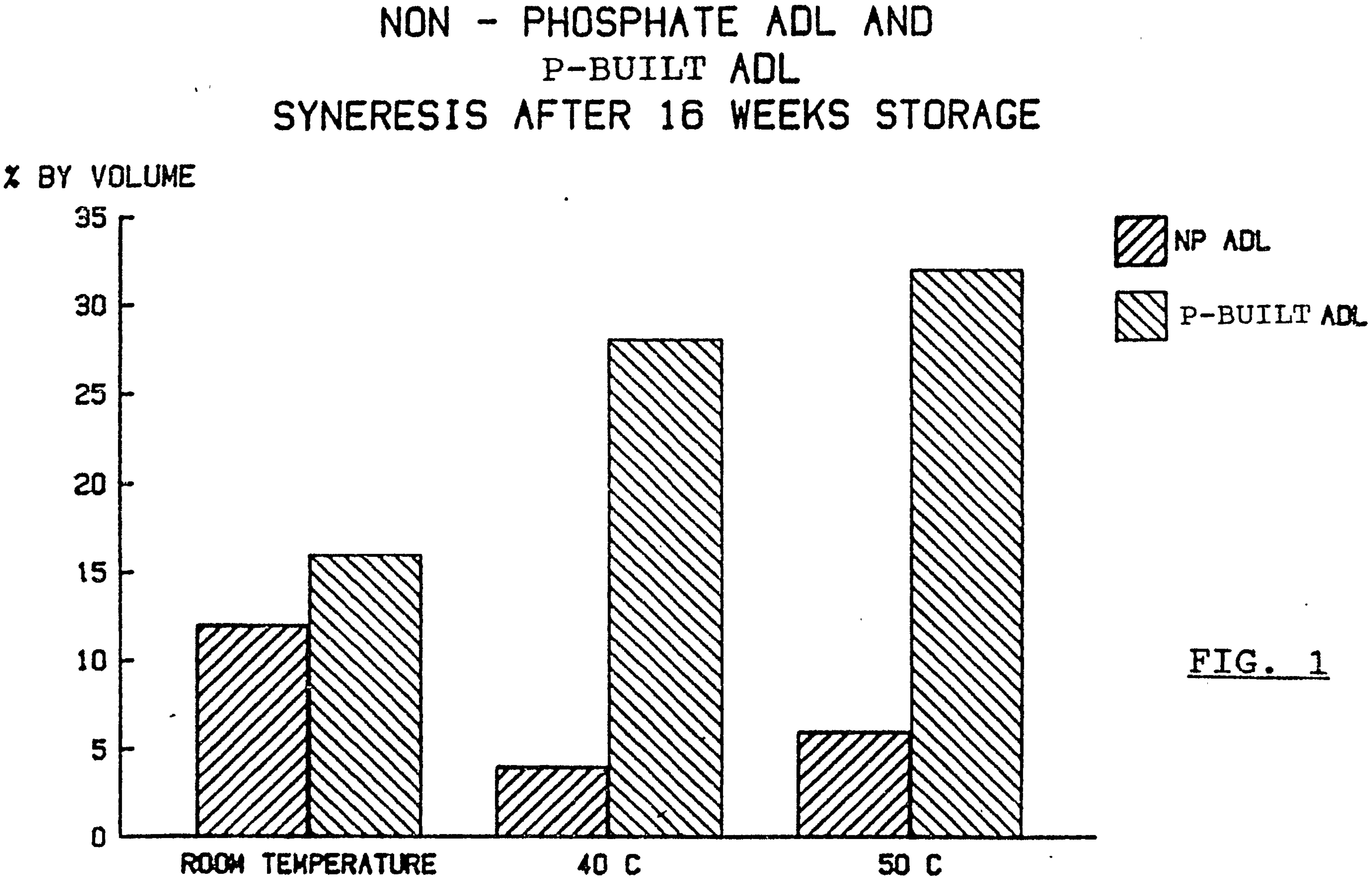
11. A cleaning composition according to claim 1 further comprising 0.05-0.5% of an opacifying agent.

12. A method of producing the thixotropic aqueous cleaning composition as claimed in claim 1 comprising:
(a) providing a vessel containing substantially all of the water needed for the composition at or slightly below room temperature;
(b) adding the clay to the water in the vessel to form a slurry in the vessel;
(c) heating the water to about 40° C and maintaining it at that elevated level for about 40 minutes;
(d) optionally adding polymeric thickener to the slurry and stirring for about 30 minutes.
(e) adding silicate to the vessel followed by up to 15 minutes of mixing;
(f) adding builder to the vessel followed by up to 15 minutes of mixing;
(g) cooling the slurry in the vessel to below 30° C; and
(h) adding bleach to the slurry in the vessel with mixing.

13. A method of producing the thixotropic aqueous cleaning composition as claimed in claim 12 wherein the builder is a low molecular weight polycarboxylic acid or salt thereof and wherein up to about 10% of this builder material as weight% of total clay present in the composition is added to the water in the vessel prior to addition of any clay thereto.

14. A method of cleaning soiled food utensils comprising:
(a) forming an aqueous solution of the composition according to claim 1;
(b) exposing soiled food utensils to the aqueous solution under agitation in an automatic dishwashing machine; and
(c) rinsing the food utensils.

15. The use of a combination of 1-15 wt% layered clay having a particle size 0.001 to 1.0 micron and 0.1-5 wt% polymeric thickener in a weight ratio of 40:1 to 5:1 in an aqueous liquid cleaning combination formulated to have an initial available chlorine level of 0.1-5% in order to reduce loss of chlorine bleach activity.



NON - PHOSPHATE ADL AND
P-BUILT ADL
SYNERESIS AFTER 16 WEEKS STORAGE

FIG. 1

NON-PHOSPHATE ADL STRUCTURING SYSTEM
EFFECT OF LAPONITE LEVEL ON RHEOLOGY

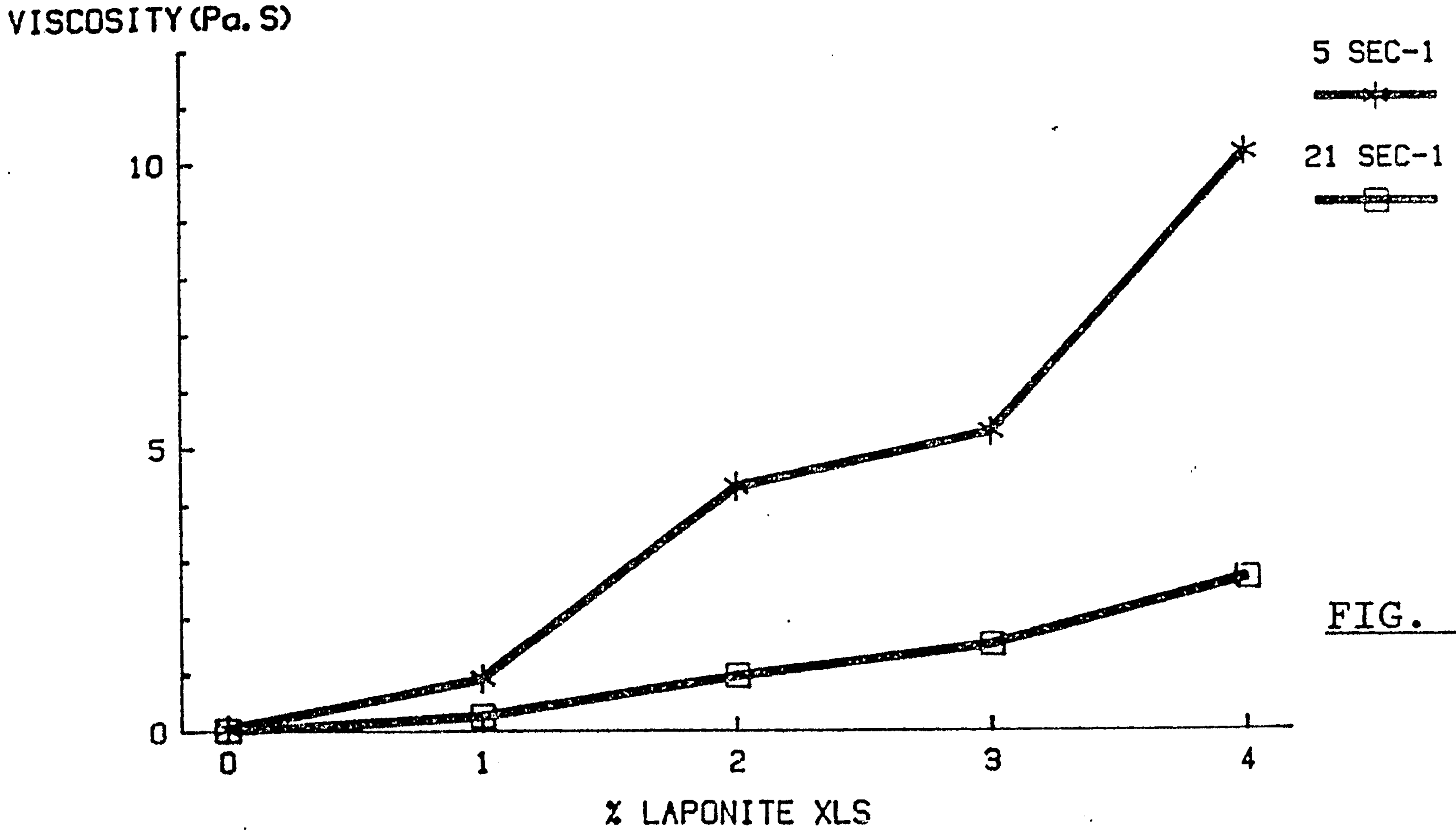


FIG. 2

NON-PHOSPHATE ADL STRUCTURING SYSTEM
EFFECT OF CARBOPOL LEVEL ON RHEOLOGY

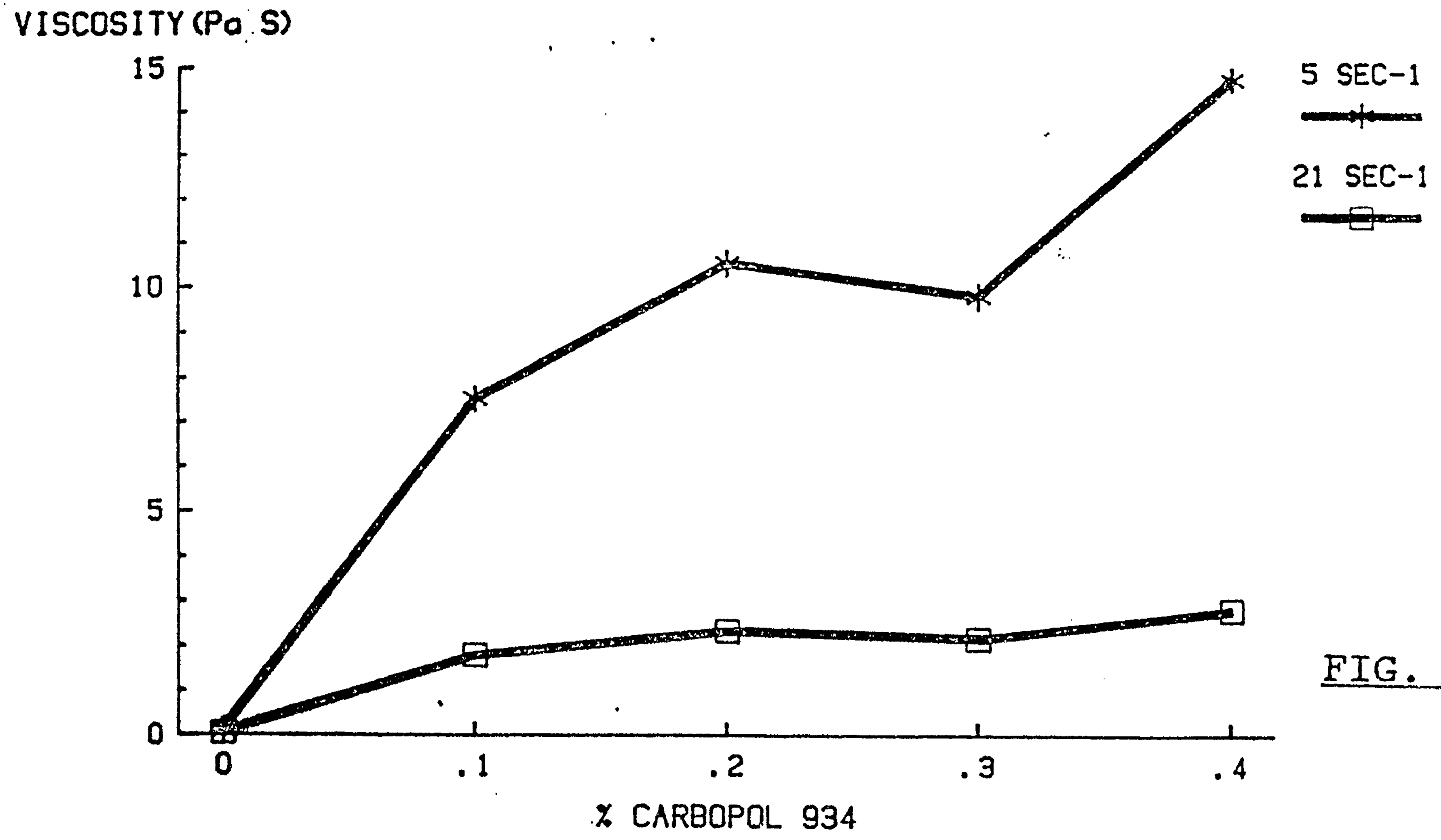


FIG. 3

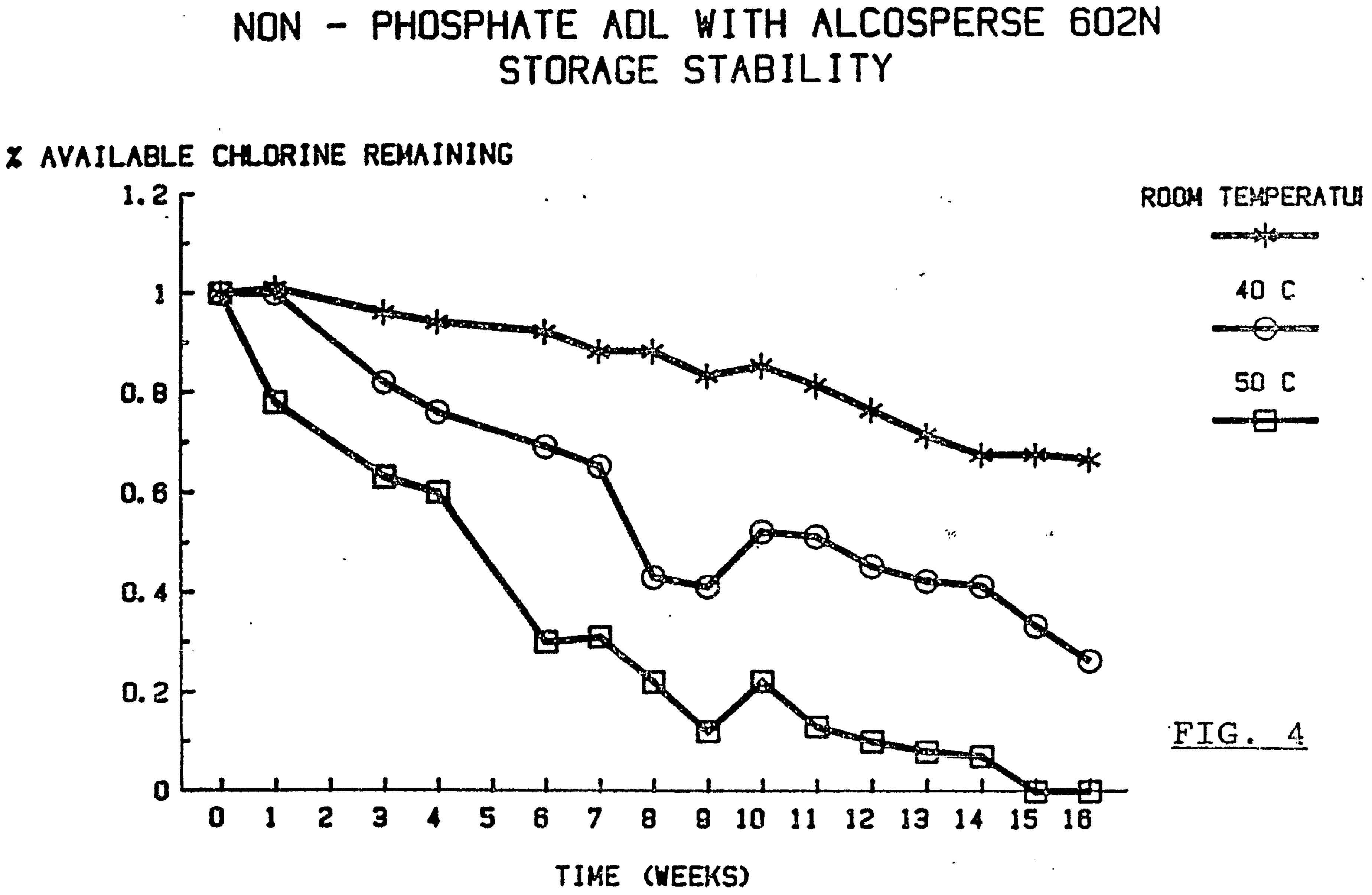

NON - PHOSPHATE ADL WITH ALCOSPERSE 602N
STORAGE STABILITY
% AVAILABLE CHLORINE REMAINING
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
TIME (WEEKS)
ROOM TEMPERATU
40 C
50 C

FIG. 4

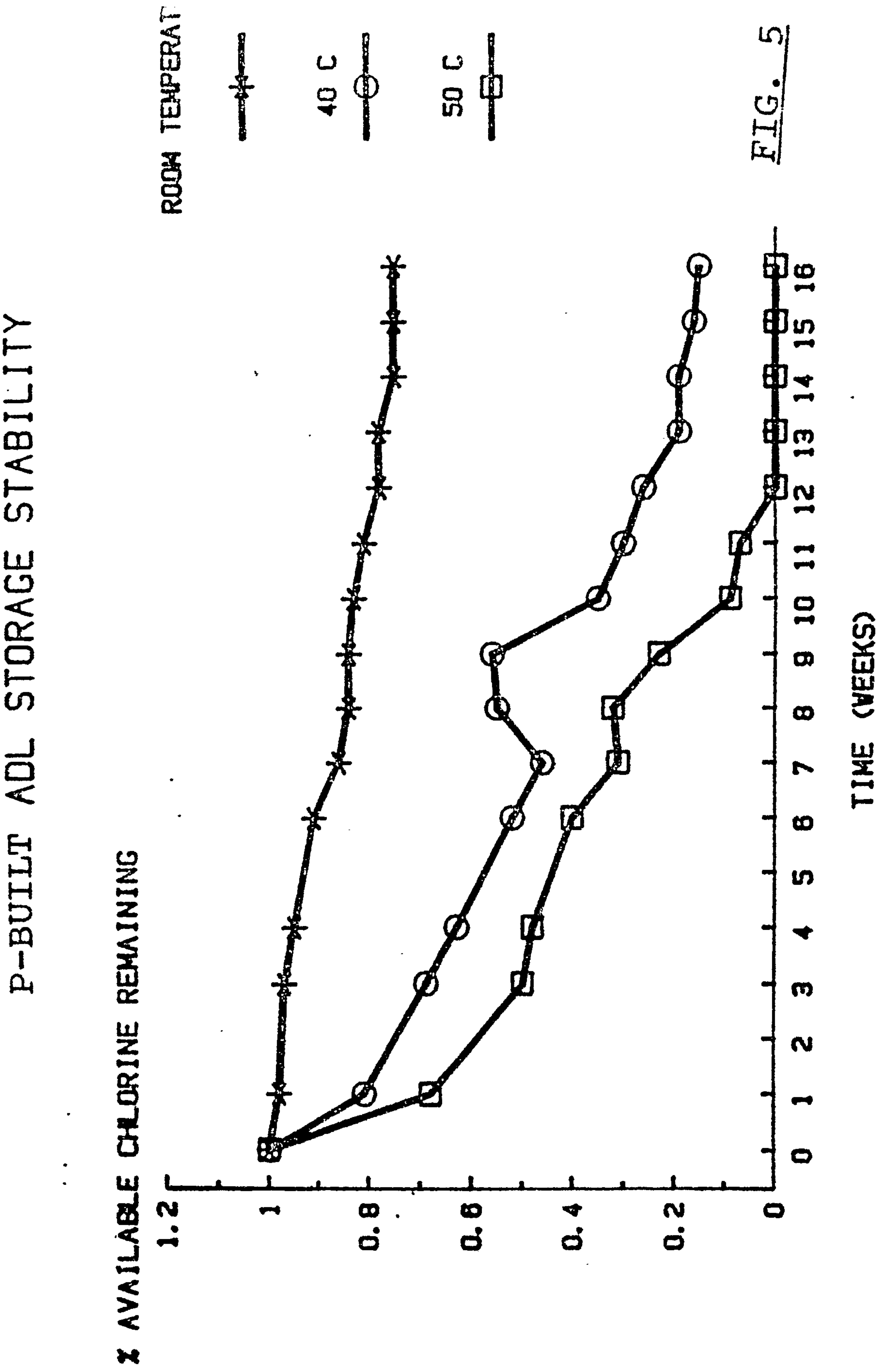

P-BUILT ADL STORAGE STABILITY
% AVAILABLE CHLORINE REMAINING
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
TIME (WEEKS)
ROOM TEMPERAT
40 C
50 C

FIG. 5

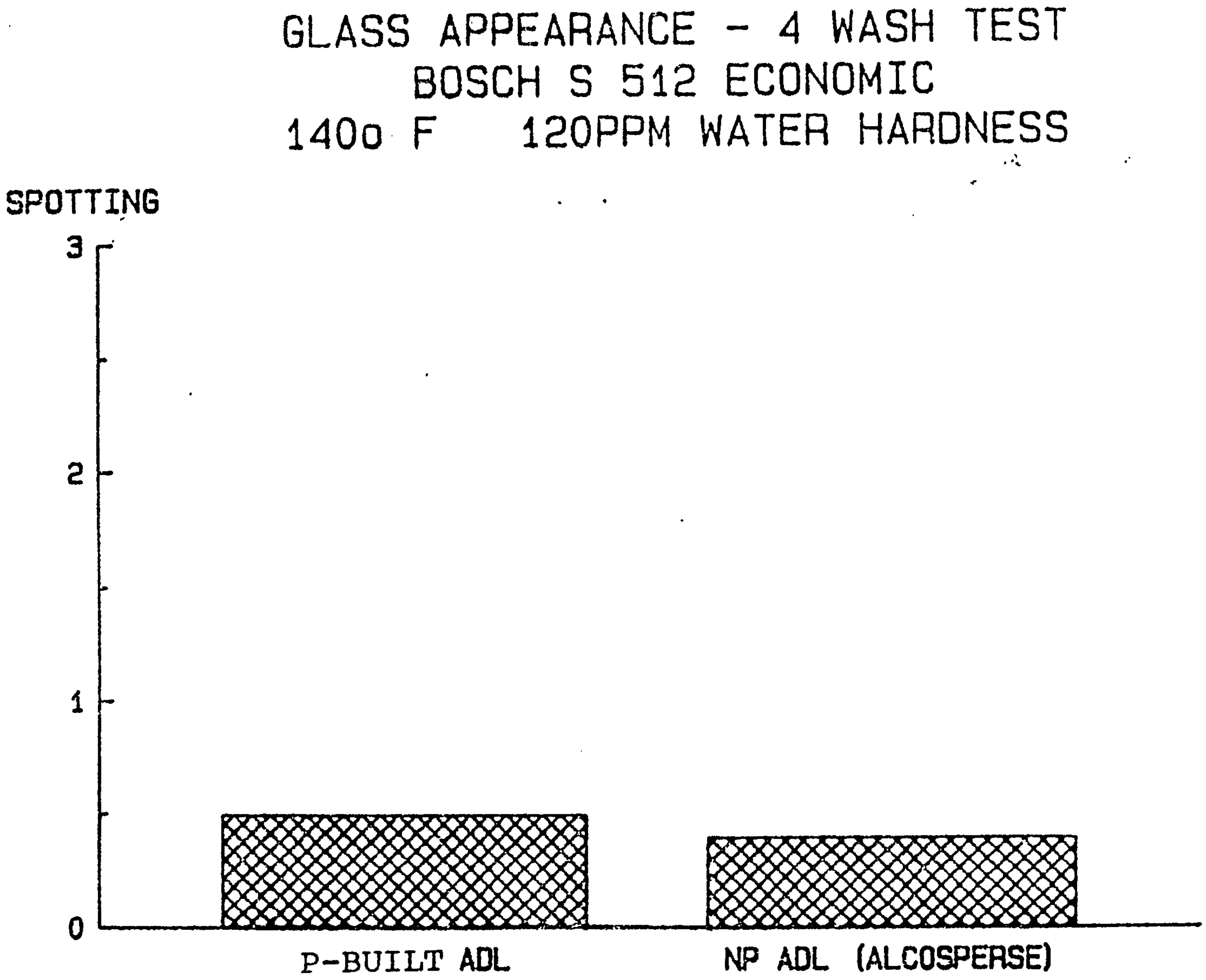

GLASS APPEARANCE - 4 WASH TEST
BOSCH S 512 ECONOMIC
140o F 120PPM WATER HARDNESS
SPOTTING
3
2
1
0
P-BUILT ADL
NP ADL (ALCOSPERSE)

FIG. 6

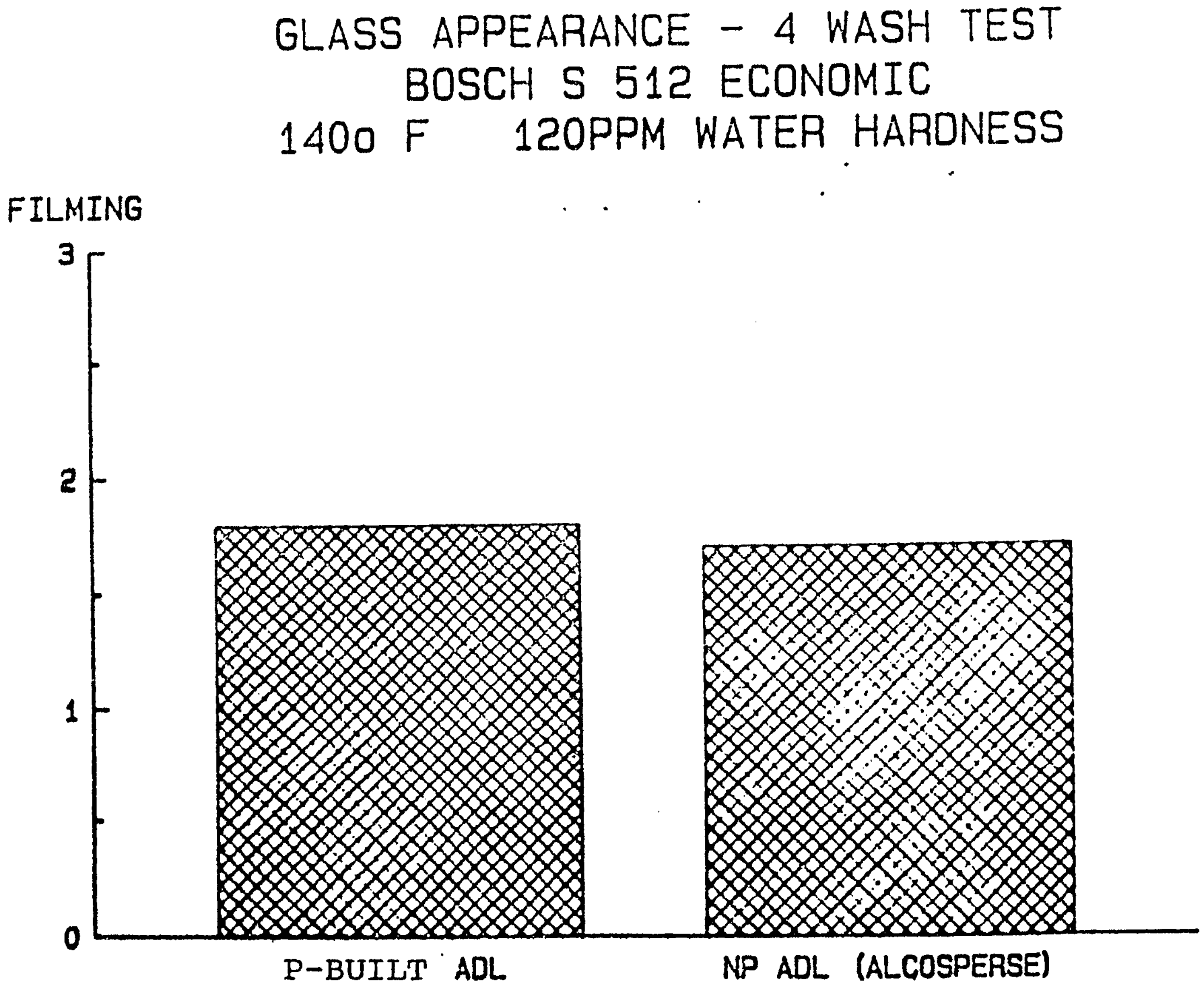

GLASS APPEARANCE - 4 WASH TEST
BOSCH S 512 ECONOMIC
140o F 120PPM WATER HARDNESS
FILMING
3
2
1
0
P-BUILT ADL
NP ADL (ALCOSPERSE)

FIG. 7

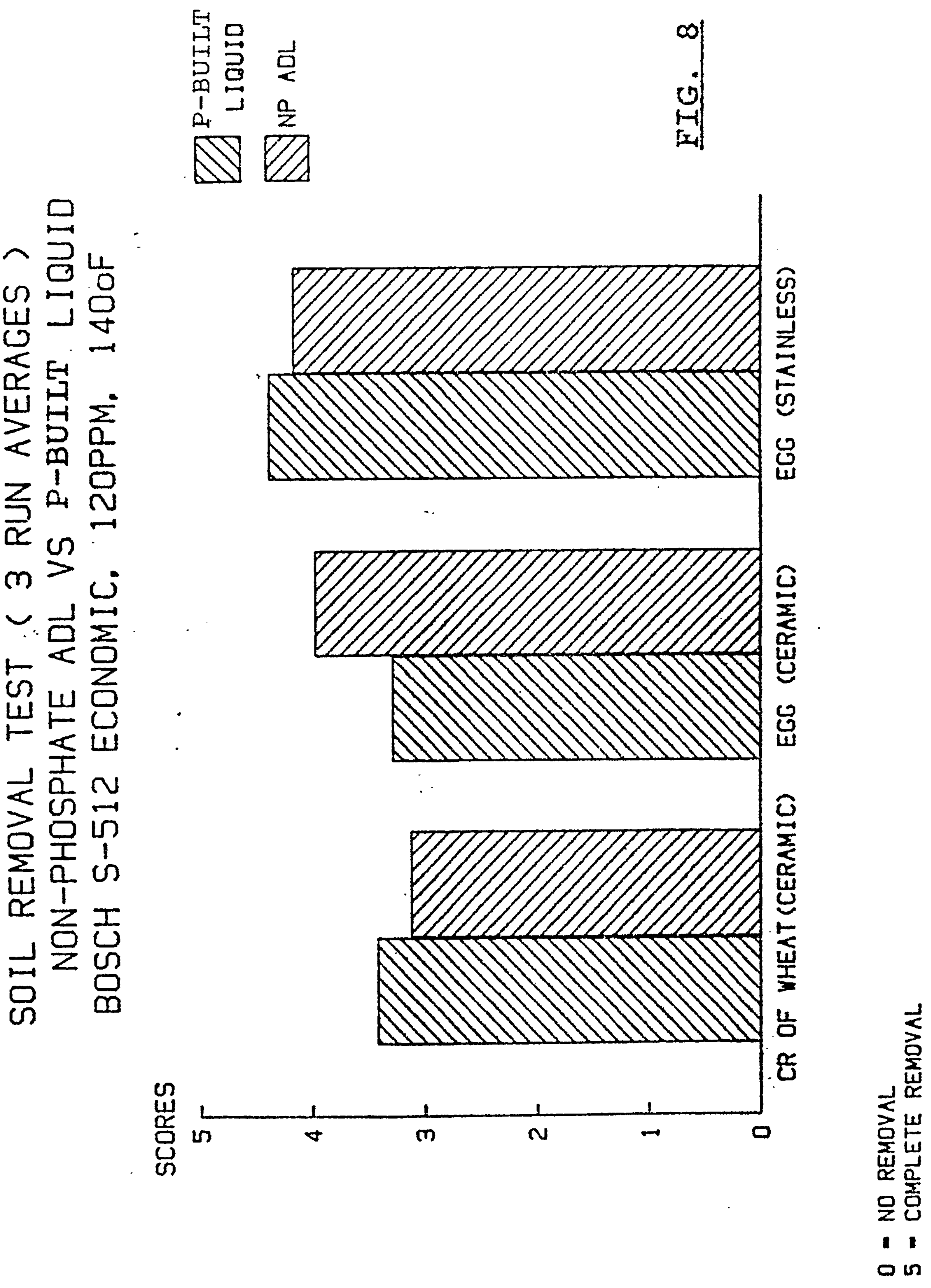

SOIL REMOVAL TEST (3 RUN AVERAGES)
NON-PHOSPHATE ADL VS P-BUILT LIQUID
BOSCH S-512 ECONOMIC, 120PPM, 140oF
P-BUILT LIQUID
NP ADL
SCORES
5
4
3
2
1
0
CR OF WHEAT (CERAMIC)
EGG (CERAMIC)
EGG (STAINLESS)
0 = NO REMOVAL
5 = COMPLETE REMOVAL

FIG. 8