

[54] **DETERGENT SLURRY COMPOSITIONS**
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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 99,081, Dec. 17, 1970, abandoned.

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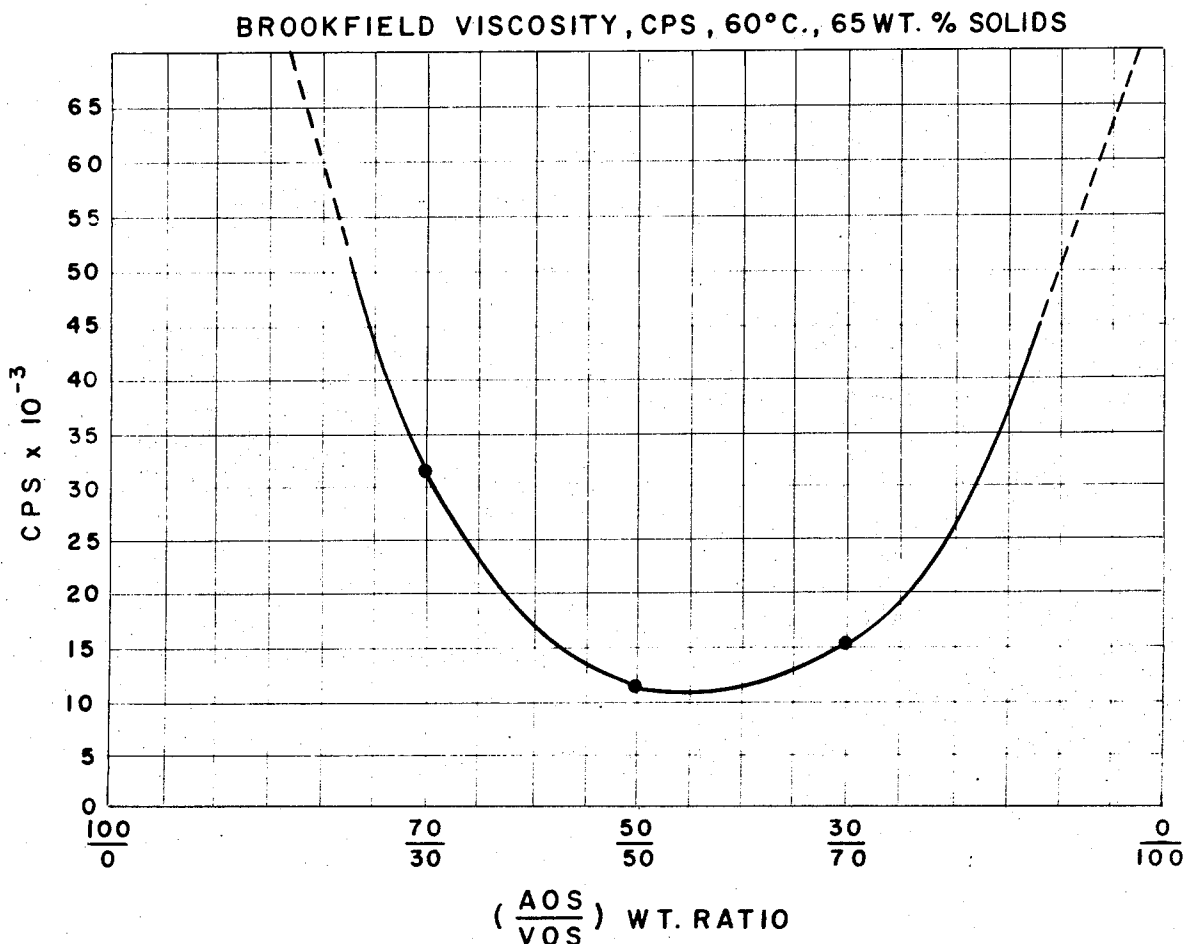
[57] ABSTRACT

A novel detergent slurry composition, also known as a crutcher slurry, comprising alpha-olefin sulfonates is provided by incorporating significant amounts of sulfonated vinylidene-olefins whereby the resulting composition is characterized by reduced viscosity.

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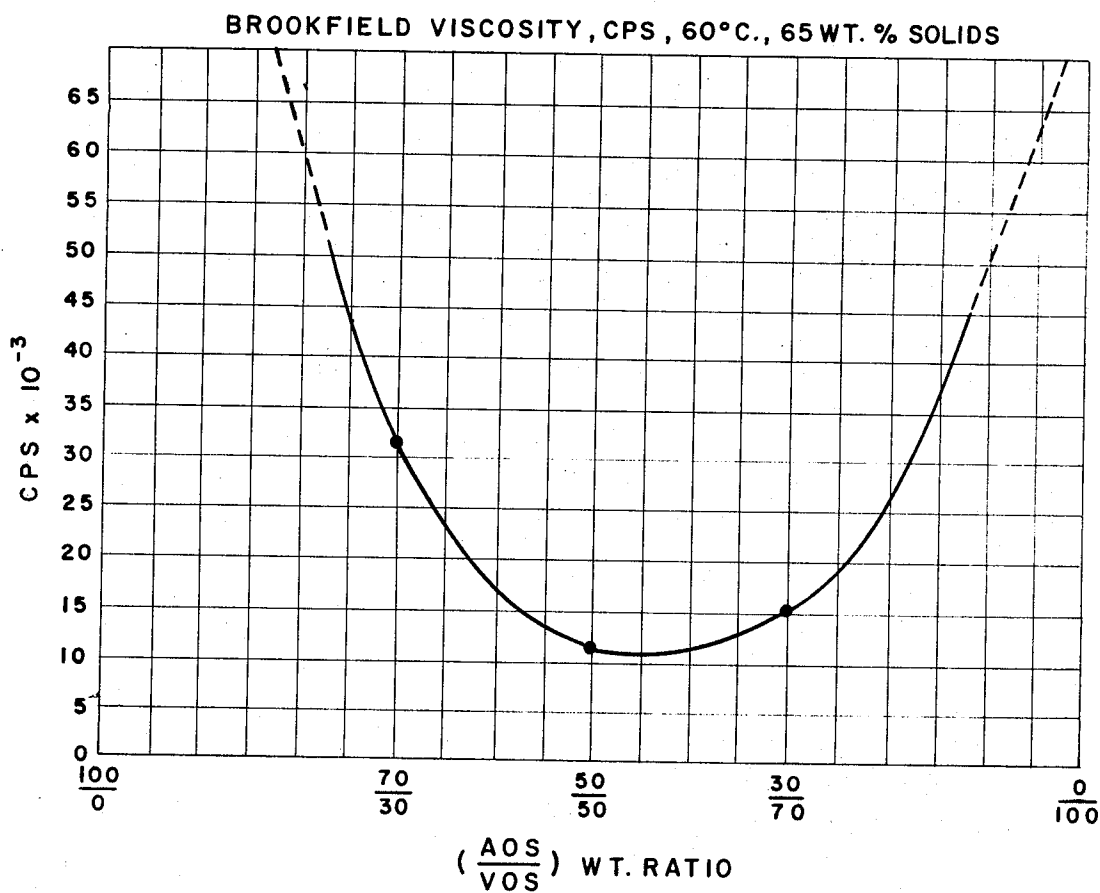
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4 Claims, 1 Drawing Figure



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DETERGENT SLURRY COMPOSITIONS

This is a continuation-in-part of U. S. Pat. application Ser. No. 99,081; filed Dec. 17, 1970, now abandoned; Floyd Edward Bentley and Harold George Waddill, inventors; entitled "Detergent Slurry Compositions."

This invention relates to a method for reducing the viscosity of detergent slurries containing alpha-olefin sulfonates by means of using sulfonated vinylidene-olefins. This invention further relates to compositions of detergent slurries containing sulfonated alpha-olefins and sulfonated vinylidene olefins.

Built detergent compositions are well known and have traditionally been prepared by forming a finished detergent slurry containing wash-active ingredients and various additives and by spray-drying the slurry to form powdered detergents.

The detergent slurry composition, also known as a crutcher slurry, contains in addition to wash-active components detergent builders or other additives which are typically employed as detergent aids. The use of additives and the like to improve the overall performance or aesthetic appeal of the formulations is widely employed. Thus, in a typical process, after the built detergent slurry is well blended, the slurry is dried in a conventional spray dryer via conventional techniques. Spray drying is, of course, an old art and is typically disclosed in U. S. Pat. No. 1,652,900.

In spray drying a built detergent slurry it is advantageous from a productivity standpoint to have as high a solids content in the crutcher slurry as can be feasibly handled. A few percent increase in the solids level of the slurry adds up to a significant monetary savings in the overall process of producing spray dried detergents. The crutcher slurry, however, at the very least must be a pumpable mixture. It is generally preferred by the industry that crutcher slurries prepared for spray drying have a viscosity of about 40,000 cps. or below.

It is also well known that the use of alpha-olefin sulfonates comprising from about eight to 24 carbon atoms per molecule, especially those comprising from about 12 to 22 carbon atoms per molecule, are enjoying wide acceptance as detergent ingredients because of their biodegradability and detergent effectiveness.

Unfortunately, however, it has been found that built crutcher slurries formed from the stated alpha-olefin sulfonates are very viscous which makes their industrial utilization difficult and at a 65 percent by weight solids level they are actually often impossible to handle.

Accordingly, it is an objective of the present invention to provide an improved detergent crutcher slurry containing alpha-olefin sulfonates characterized by a high solids level and a reduced viscosity.

It has now been discovered that the viscosity of a crutcher slurry comprising sulfonated alpha-olefins can be surprisingly reduced by incorporating into the slurry significant quantities of sulfonated vinylidene-olefins. The incorporation of the vinylidene-olefin sulfonates provides a slurry that is high in solids level and easily handled thereby enabling more efficient preparation of spray-dried detergents.

The FIGURE is a graphic illustration representative of the synergistic effects obtained according to our invention as explained in Example I which follows.

The incorporation of sulfonated vinylidene-olefins not only provides a vastly improved slurry, its use enables preparation of very effective detergents.

We have found that the incorporation of sulfonated vinylidene-olefins or a replacement of significant amounts of sulfonated alpha-olefins by sulfonated vinylidene-olefins gave a surprising drop in the viscosity of aqueous built detergent slurries which was not predictable from the viscosities of the crutcher slurries containing the stated individual components. The viscosity-reducing effect obtained according to this invention is therefore synergistic.

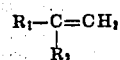
Thus, the detergent slurry composition consists of about 50 to about 70 wt. % solids, the remainder being water, the solids portion of the slurry contains about 5 to 45 wt. % preferably 10 to 25 wt. % of active ingredient, i.e., wash-active materials and 95 to 55 wt. %, preferably 90 to 75 wt. %, detergent builders or other additives. The active ingredient portion, in accordance with this invention, comprises about 25 to 75 wt. %, preferably about 30 to 70 wt. %, sulfonated alpha-olefins and about 75 to 25 wt. %, preferably 70 to 30 wt. %, sulfonated vinylidene-olefins. In the most preferred embodiment, the active ingredient portion comprises greater than 50 wt. % sulfonated vinylidene-olefins and less than 50 wt. % sulfonated alpha-olefins. The active ingredient portion of the built detergent slurry can include additional wash-active materials if desired such as anionic or nonionic surface-active wash-active materials in addition to the sulfonated alpha-olefins and the sulfonated vinylidene-olefins.

Due to their reduced viscosity the crutcher slurries formulated according to this invention are particularly suitable for the incorporation of other wash-active materials and additives customarily employed in making washing and cleansing agents.

The compositions of this invention thus comprise a crutcher slurry containing about 50 to 70 percent by weight solids, preferably 60 to 65 percent by weight, the remainder water. The stated solids portion comprises about 5 to 45, preferably about 10 to 25 wt. % wash-active material wherein the wash-active material comprises about 25 to 75 wt. % sulfonated alpha-olefins and about 75 to 25 wt. % sulfonated vinylidene-olefins. Accordingly, the stated solids portion comprises about 95 to 55 wt. %, preferably about 90 to 75 wt. % detergent builders and other additives as herein discussed.

The sulfonated vinylidene-olefins, and admixtures thereof, which serve to reduce the viscosity of crutcher slurries containing alpha-olefin sulfonates are employed in the form of salts. The cation or salt portion is preferably sodium, potassium, ammonium, or an organic base such as mono-, di-, or triethanolamine. Mixtures of the stated salts can, of course, be employed.

The sulfonated vinylidene-olefins are obtained by conventional sulfonation of vinylidene-olefins which can be characterized by the following representative formula:



wherein R_1 and R_2 , taken individually, represent a C_1 to C_{10} alkyl and wherein the total carbon atoms per molecule are about 12 to 20.

Vinylidene-olefins can be prepared, for example, by dimerizing C_6 to C_{10} alpha-olefins, or admixtures thereof, such as in the presence of aluminum alkyl, such as triethylaluminum as described in U. S. Pat. No.

2,695,327. Exemplary vinylidene-olefins are 2-hexyldecene-1, 2-octyldecene-1, 2-octyl-dodecene-1, and the like.

The sulfonated alpha-olefin component and admixtures thereof, as hereinbefore stated, contain about 12 to 22 carbon atoms per molecule. A conventional source for the alphaolefin can be by the conversion of ethylene via a combined growth-displacement reaction using the Ziegler-type polymerization catalyst. The resultant alpha-olefin mixture, like the vinylidene-olefins, can be fractionated and the olefin fraction desired, ranging from about C_{12} to C_{22} , recovered and subsequently sulfonated.

The sulfonation process for the vinylidene and alpha-olefins is by conventional methods such as described in U. S. Pat No. 3,169,142. The vinylidene and alphaolefins can be cosulfonated if desired, as a mixture, or admixed following individual sulfonation.

The alpha- and vinylidene-olefin sulfonates employed according to this invention need not be entirely pure. They can, accordingly, be prepared from olefin feeds that contain small amounts, e.g., not more than 10 wt. % of internal olefins, paraffins, diolefins, olefins containing carbon atoms per molecule greater than C_{22} or less than C_{12} , mixtures thereof, and the like. Sulfonation with sulfur trioxide is the preferred method. The use of other sulfonating agents can be employed if desired. It is generally preferred when cosulfonating to employ a falling film reactor wherein sulfonation is accomplished by using vaporized or gaseous SO_3 which has been diluted to about 2 to 5 percent by volume concentration with inert gas at a temperature of about 20°C. to 80°C., preferably from about 25°C. to 75°C., using a mol ratio of sulfur trioxide to olefin from about 1.0:1.0 to 1.6:1.0, preferably 1.10:1.0 to 1.4:1.0, at either atmospheric or superatmospheric pressures. The conventional sulfonation step can be followed by an aging step of from about 0 to 24 hours at a temperature of about 25° to 50°C. The acidic slurry from the cosulfonation reaction is then neutralized with a strong base and diluted with water to the desired solids level. A strong base is added in an amount equivalent to the sulfonic acid, sultones, plus free sulfur trioxide in the reactor effluent, generally using about a 2 to 5 percent excess. Following neutralization, the slurry is saponified by heating to temperatures from about 100° to 200°C., preferably about 125° to 160°C., for about ½ to 4 hours either at atmospheric pressure or superatmospheric pressure.

The preparation of the crutcher slurry is by conventional methods. The sulfonated vinylidene-olefin can be added to the sulfonated alpha-olefin as the slurry as directly produced from the sulfonation reaction. If the components were cosulfonated, the builders or other additives and active ingredients can be merely incorporated therewith, and the solids content of the resultant slurry adjusted by the addition of water. If desired, of course, the sulfonates can be further refined prior to preparation of the crutcher slurry.

The builders or other additives can be incorporated such as by their introduction during neutralization or after saponification if desired. In order to prevent precipitates from forming, such as insoluble silicates, it is preferred that the additives and other builders be incorporated subsequent to neutralization. The built detergent slurry, after it is well blended, is passed to a conventional spray tower and spray dried according to

conventional techniques in batch or continuous processes. The crutcher slurry if prepared according to our invention is characterized by a high solids level and a reduced viscosity enabling easy handling and high productivity in producing detergents.

Some typical detergent builders or other additives usefully employed in practicing this invention are representatively disclosed herein. They include inorganic detergent builders, organic builders and/or chelate formers, foam stabilizers, anti-redeposition agents, hydrotropes, buffering agents, and the like. Preferably, detergent builders comprising sodium tripolyphosphate, sodium citrate, sodium carbonate, disodium oxydiacetate, or admixtures thereof, are employed in amounts sufficient to comprise about 15 to 65 wt. % of the total weight of the stated solids portion.

Inorganic compounds can be included in the built detergent composition to augment the deterative portion of the composition and representatively include such compounds as the alkali metal carbonates, such as potassium carbonate; borates, such as potassium tetraborate; silicates, such as sodium silicate. Phosphates, such as pyro, poly-, meta-, or orthophosphates are suitable. Sodium pyrophosphate, and the like, is exemplary.

Organic builders and/or chelate formers can also be used with the aforestated inorganic alkaline builders and include such materials as the alkali metal salts of phytic acid; alkali metal, ammonium or substituted ammonium aminopolycarboxylate, such as sodium and potassium N-(2-hydroxyethyl)ethylenediamine triacetates, sodium and potassium nitrilotriacetates and sodium potassium and triethanolammonium-N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. Other valuable polycarboxylate builder compounds are the sodium and potassium salts of polymaleate, polyacrylate and polymethacrylate. Other organic builders such as the polyphosphonates such as sodium and potassium salts of ethane-1,1,1-diphosphonate, sodium and potassium salts of methylene diphosphonate, sodium and potassium salts of ethylene diphosphonate, and sodium and potassium salts of ethane-1,1,2-triphosphonate are exemplary. Alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanediphosphonic acid, carbonyl diphosphonic acid, ethane-1-hydroxy, 1,1,2-triphosphonic acid, and the like, are also representative.

Foam stabilizers can also be employed as additives such as the alkanol amides of fatty acids such as the isopropanol amide of lauric acid and the ethanol amide of lauric acid, water-soluble alkaline salts of N-alkylimino-diacetic acid, and the like.

Anti-redeposition agents and organic high-molecular colloidal substances such as water-soluble derivatives of cellulose and starch exemplified by sodium carboxymethyl cellulose are also suitable.

Various hydrotropes can be added if desired to improve the compatibility of the various ingredients employed. Hydrotropes such as benzene sulfonate, xylene sulfonate, toluene sulfonate or their salts such as ethanolammonium, diethanolammonium, and triethanolammonium and especially as the alkali metal potassium or sodium salts are suitable.

Various miscellaneous agents such as buffering agents, anticorrosion agents, water softeners, wetting agents, optical brighteners, chemical bleaching agents, resin stabilizers, dyes and pigments, germicides and an-

tibacterial agents, and the like, as is customary, can be suitably employed.

In addition to the aforestated additives and builders that are suitable for incorporation with the sulfonated alphaolefin and sulfonated vinylidene-olefin components of this invention; various other wash-active cleaning agents can be suitably incorporated in the crutcher slurry.

Exemplary wash-active materials include anionic, nonionic, ampholytic and Zwitterionic detergent components. The alkali soaps of fatty acids can be suitably employed as well as the synthetic nonsoap detergent materials. Exemplary wash-active materials are disclosed in U. S. Pat. Nos. 3,159,581 and 3,213,030.

All of the aforementioned U. S. patents are hereby incorporated by reference thereto.

Illustrative of the foregoing discussion and description and not to be interpreted as a limitation on the scope thereof or on the materials herein employed, the following examples are presented to illustrate the viscosity-reducing effect of the vinylidene-olefin sulfonates in typical built detergent slurries, commonly known as crutcher slurries.

EXAMPLE I

Crutcher slurries were formulated using the following typical detergent formulation:

Active ingredient	Wt. %
Sodium tripolyphosphate	48.20
Sodium silicate	8.42
Sodium carboxymethyl cellulose	1.20
Sodium sulfate	28.90
Sodium xylene sulfonate	1.28

The ingredients were well blended with water to form a 65 wt. % solids slurry and the viscosity of each slurry at 60°C. was measured on the Brookfield viscometer. The composition and concentration of active ingredient as well as the results are reported in Table 1 and graphically depicted in the figure.

TABLE 1

Active Ingredient, Wt. %	1	Run No. 2	34	5
Alpha-olefin sulfonate ⁽¹⁾	100	0	7030	50
Vinylidene-olefin sulfonate ⁽²⁾	0	100	3070	50
Viscosity cps. at 60°C.	2,000,000	120,000	31,150,000	11,200
(1) 41 wt. % C ₁₆ , 33 wt. % C ₁₈ , 26 wt. % C ₂₀ - sodium salt.				
(2) 22.5 wt. % C ₁₆ , 57.5 wt. % C ₁₈ , 19.4 wt. % C ₂₀ - sodium salt.				

EXAMPLE II

The above example was similarly repeated except that viscosities were determined on crutcher slurries at various solids levels.

The identified formulation employed in Example I was used. The viscosity results are reported in Table 2.

TABLE 2

Active Ingredient, Wt. %	50%	60%	65%
Alpha-olefin sulfonate ⁽¹⁾	168,000	2,000,000	2,000,000
Alpha-olefin sulfonate vinylidene-olefin sulfonate mixture ⁽²⁾	400	2,050	11,000
(1) Same as reported in Table 1.			
(2) 44.3 wt. % alpha-olefin sulfonate (sodium salt)-18 wt. % C ₁₆ , 14.4 wt. % C ₁₈ , 11.8 wt. % C ₂₀ ; 55.7 wt. % vinylidene-olefin sulfonate (sodium salt) 17.1 wt. % C ₁₆ , 29.2 wt. % C ₁₈ , 9.4 wt. % C ₂₀ .			

EXAMPLE III

A crutcher slurry was formulated to yield the following dry powder composition:

Active ingredient	Wt. %
Sodium tripolyphosphate	40.0
Sodium silicate	7.0
Sodium carboxymethyl cellulose	0.5
Sodium sulfate	30.0
Water	7.5

The ingredients were blended with water to form slurries as reported in Table 3. The viscosity of each slurry at 60°C. was measured as in previous examples and is reported in Table 3.

TABLE 3

Active Ingredient, Wt. %	50%	60%	65%
Alpha-olefin sulfonate vinylidene-olefin sulfonate mixture ⁽¹⁾	2,000	3,600	8,640
Alpha-olefin sulfonate ⁽²⁾	3,800	82,000	>1,000,000
(1) 13.10 wt. % C ₁₂ , 14.00 wt. % C ₁₆ , 23.80 wt. % C ₁₈ and 7.65 wt. % C ₂₀ vinylidene-olefin sulfonates; 14.73 wt. % C ₁₆ , 11.82 wt. % C ₁₈ , 9.48 wt. % C ₂₀ and 5.54 wt. % C ₂₂ alpha-olefin sulfonates.			
(2) 13.10 wt. % C ₁₂ , 28.7 wt. % C ₁₆ , 35.6 wt. % C ₁₈ , 17.1 wt. % C ₂₀ and 5.5 wt. % C ₂₂ alpha-olefin sulfonates.			

The foregoing examples effectively demonstrate that the addition of sulfonated vinylidene-olefins or the replacement of alpha-olefin sulfonates with sulfonated vinylideneolefins produces a surprising and significant drop in the viscosity of the aqueous crutcher slurries and demonstrates a synergistic effect of these two components to provide a viscosityreducing effect.

EXAMPLE IV

Crutcher slurries were formulated using the following dry powder compositions:

Formula	I	II	III	IV	V
Active ingredient (sodium salt-olefin sulfonate) ¹	15.0	15.0	15.0	15.0	15.0
Sodium carbonate	30.0	30.0	30.0	30.0	30.0
Sodium tripolyphosphate	5.0	10.0	10.0	10.0	10.0
Sodium citrate					25.0
Disodium oxydiacetate				30.0	30.0
Sodium silicate	10.0	7.0	7.0	10.0	7.0
Carboxymethyl cellulose	0.5	0.5	0.5	0.5	0.5
Sodium sulfate	37.0	35.0	30.0	37.0	45.0
Water	7.5	7.5	7.5	7.5	7.5

¹ When employed, the alpha-olefin sulfonate had the following composition: 36 wt. percent C₁₆, 23 wt. percent C₁₈, 22 wt. percent C₂₀, 14 wt. percent C₂₂; when employed, the vinylidene-olefin sulfonate had the following composition: 13.3 wt. percent C₁₂, 23.7 wt. percent C₁₆, 34 wt. percent C₁₈, 23.4 wt. percent C₂₀, 8.5 wt. percent C₂₂.

The various ingredients in the above formulations I to V were well blended with water to form 60 wt. % solids slurries in formulations I-III and 65 wt. % solids slurries in formulations IV and V. The viscosities of each of the above-mentioned slurries were then determined when the active ingredient employed was an all alpha-olefin sulfonate, an all vinylidene-olefin sulfonate and lastly wherein the active ingredient was a mixture of alpha- and vinylidene-olefin sulfonates. The results are reported in Table 4.

TABLE 4

Run No.	Active Ingredient	Wt. percent	Viscosity, cps. at 60° C. (Brookfield viscometer)				
			Formula I	Formula II	Formula III	Formula IV	Formula V
1	Alpha-olefin sulfonate	100.0	6,800	3,640	16,000	3,320	4,500
2	Vinylidene-olefin sulfonate	100.0	(1)	(1)	(1)	240	~800
3	Alpha/vinylidene-olefin sulfonate	2 40/60	540	1,030	~2,000	930	1,000

¹ The solids coagulated in each instance to form little balls and was not an acceptable slurry. Viscosity determination meaningless.
² Approximately 40 wt. percent alpha-olefin sulfonate, 60 wt. percent vinylidene-olefin sulfonate.

EXAMPLE V

Formula I of the above example was employed and the example similarly repeated except that viscosities were determined on crutcher slurries at various solids levels. The viscosity results are reported in Table 5.

TABLE 5

Active Ingredient	60%	Viscosity ⁽¹⁾ Wt. % solids of crutcher slurry	
		65%	70%
Alpha-olefin sulfonate ⁽¹⁾	6,800	25,000	37,500
Vinylidene-olefin sulfonate ⁽¹⁾	(2)	(2)	(2)
Alpha/vinylidene-olefin sulfonate ⁽¹⁾	540	360	1,200 ⁽³⁾

(1) Same as reported in Table 4.
(2) Solids coagulated into balls.
(3) Spindle not wet properly, viscosity value not exact.

The preceding examples can be repeated with similar success by substituting the generically and specifically described reactants and conditions of this invention with those employed in the examples. As will be evident to those skilled in the art various modifications of this invention can be made or followed in light of the discussion and disclosure herein set forth without departing from the spirit or the scope thereof.

We claim:

1. A process for reducing the viscosity of a crutcher slurry containing from about 50 percent to about 70 percent by weight solids, wherein said solids comprise a wash-active material and detergent builders and the remainder water, wherein about 5 to 45 wt. % of the stated solids is wash-active material and wherein the stated wash-active material is from about 25% to 75% by weight sulfonated alpha-olefin containing about 12 to 24 carbon atoms per molecule comprising incorporating a viscosity reducing agent consisting of sulfonated vinylidene-olefins containing about 12 to 20 carbon atoms per molecule into said slurry to reduce the viscosity thereof in an amount to provide about 75% to 25% by weight sulfonated vinylidene-olefins based on the total weight of the stated wash-active material.
2. The process according to claim 1 wherein said wash-active material comprises more than 50 percent by weight sulfonated vinylidene-olefins and less than 50 wt. % sulfonated alpha-olefins.
3. The process according to claim 2 wherein about 15 to 65 percent by weight of the stated solids comprise a detergent builder selected from sodium tripolyphosphate, sodium citrate, sodium carbonate, sodium oxydiacetate, or admixtures thereof.
4. The process according to claim 3 wherein the stated solids level is from about 60 to 65 wt. % and wherein the stated crutcher slurry has a viscosity of 40,000 cps. or below.

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