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(54) Titre : METHODE DE PERFECTIONNEMENT DES EPAISSISSANTS POUR SYSTEMES AQUEUX

(54) Title: METHOD FOR IMPROVING THICKENERS FOR AQUEOUS SYSTEMS

(57) **Abrégé/Abstract:**

A method is provided for improving thickeners used in aqueous system. The improvement is directed to the elimination of organic cosolvents which are conventionally added to aqueous solutions of certain hydrophobic thickeners. This method involves the reversible complexation of cyclodextrin compounds with hydrophobia moieties on the thickener molecule to suppress the viscosity of the aqueous solution containing the thickener so that such the solution can be easily handled. This is followed by decomplexing the cyclodextrin from the thickener to permit the thickener to perform its intended function.



ABSTRACT OF DISCLOSURE

A method is provided for improving thickeners used in aqueous system. The improvement is directed to the elimination of organic cosolvents which are conventionally added to aqueous solutions of certain hydrophobic thickeners. This method involves the reversible complexation of cyclodextrin compounds with hydrophobic moieties on the thickener molecule to suppress the viscosity of the aqueous solution containing the thickener so that such the solution can be easily handled. This is followed by decomplexing the cyclodextrin from the thickener to permit the thickener to perform its intended function.

FIELD OF THE INVENTION

This invention relates to thickeners used in aqueous systems, such as for example in aqueous latex paint formulations, and more particularly to aqueous solutions of certain hydrophobic thickeners which require the presence of organic cosolvents. More particularly, the invention is directed to the use of cyclodextrin compounds for reversibly complexing with hydrophobic moieties on the thickener molecule resulting in the suppression of the viscosity of aqueous solutions containing such thickeners.

BACKGROUND OF THE INVENTION

Aqueous systems, such as for example coatings containing emulsion polymer binders, typically employ thickeners to obtain the desired degree of viscosity needed for the proper formulation and application of the aqueous system. One general type of thickener used in aqueous systems is referred to in the art by the term "associative". Associative thickeners are so called because the mechanism by which they thicken is believed to involve hydrophobic associations between the hydrophobic species in the thickener molecules themselves and/or with other hydrophobic surfaces. A number of different types of associative thickeners are known including,

but not limited to polyurethanes, hydrophobically modified alkali soluble emulsions, hydrophobically modified hydroxyethyl cellulose or other natural products, and hydrophobically modified polyacrylamides.

Certain of these associative thickeners, such as for example the polyurethane thickeners, are sold as aqueous solutions containing organic cosolvents. The function of the organic cosolvent, such as for example propylene glycol, is to suppress the viscosity of the aqueous solution containing the associative thickener to allow for ease in its handling before its use as a thickener. While these organic cosolvents perform their intended function, they possess potential environmental, safety and health disadvantages. Viscosity suppression may also be accomplished by the use of surfactants. While this presents no specific health/environmental hazard, it does degrade formulation performance.

It would therefore be advantageous if one could develop more environmentally acceptable and safe materials which could be used in place of these organic cosolvents or surfactants.

DESCRIPTION OF THE PRIOR ART

There are many references which disclose various hydrophobic compounds which act as associative thickeners. The associative thickeners are formulated with organic cosolvents or surfactants for use in thickening aqueous latex systems.

Collo 3/00 Collo 3/00

U.S. Patents 4,155,892 and 4,079,028 are directed to polyurethane thickeners, characterized by at least three hydrophobic groups interconnected by hydrophilic polyether groups, formulated with organic cosolvents.

Collo 7/00

U.S. 4,426,485 is directed to water-soluble thermoplastic, organic polymers having a weight average molecular weight of at least about 10,000 comprising hydrophobic segments each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobic bunching comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer.

U.S. 4,496,708 is directed to water-soluble polyurethane comb polymer thickeners .

U.S. Patent 4,499,233 discloses polyurethane thickeners in solution form in a water compatible solvent.

U.S. Patent 4,180,491 also discloses urethane associative thickeners which use a non-aqueous , inert organic diluent.

Japanese Patent Disclosure No. 60-49022 describes using ethanol or surfactants with water for the dissolution of urethane associative thickeners.

None of these references, however, disclose or suggest a suitable method for providing the thickener in an aqueous solution at a handleable viscosity without the use of organic cosolvents.

It is therefore an object of the present invention to provide a method for improving associative thickeners by eliminating the need for organic cosolvents.

SUMMARY OF THE INVENTION

A method for improving associative thickeners by the addition of one or more cyclodextrin compounds to aqueous solutions containing associative thickeners is provided. The cyclodextrin compound suppresses the viscosity of aqueous solutions containing associative thickeners and eliminates the need for organic cosolvents. In addition the viscosity suppressing function of the cyclodextrin compounds is readily reversed, as needed, by the addition of a compound having an affinity for the cyclodextrin, such as for example a surfactant, thereby providing an effective associative thickener for aqueous systems. In other embodiments of the invention the cyclodextrins have been found to: improve the ease of incorporating hydrophobically modified, associative thickeners, having marginal solubility in water, into aqueous systems; to reduce the viscosity drop of associative thickener containing formulations upon the addition of colorants or surfactants to the formulation; to improve the efficiency of the associative thickener itself, thus reducing the thickener required to reach a given paint viscosity; to reduce foaming in a latex paint, and to reduce the color development problems caused by surfactants in some formulations.

DETAILED DESCRIPTION OF THE INVENTION

Cyclodextrin compounds are cyclically closed oligosaccharides with 6, 7 or 8 alpha-D-glucoses per macrocycle. The six glucose ring cyclodextrin compound is referred to as an alpha-cyclodextrin; the 7 glucose ring cyclodextrin compound is referred to as a beta-cyclodextrin, and the 8 glucose ring cyclodextrin compound is referred to as the gamma-cyclodextrin. Cyclodextrins are produced from starch of any selected plant variety, such as corn, potato, waxy maize, and the like which may be modified or unmodified starch derived from cereal or tuber origin and the amylose or amylopectin fractions thereof. The selected starch in the form of an aqueous slurry, at concentrations up to about 35 % by weight solids, is usually liquefied, as by gelatination or treatment with a liquefying enzyme such as bacterial alpha-amylase enzyme, and then subjected to treatment with a transglycosylase enzyme to form the cyclodextrins. The amount of individual alpha, beta and gamma cyclodextrins will vary depending on the selected starch, selected transglycosylase enzyme and processing conditions. Precipitation and separation of the individual cyclodextrins is described in the literature using solvent systems, inclusion compounds such as trichloroethylene and non-solvent systems utilizing selected ion exchange resins. Each of the cyclodextrins as well

as mixtures thereof are commercially available materials. Beta-cyclodextrin is the most widely used form and is known for use in the production of pharmaceuticals and foods.

The ability of cyclodextrins to form inclusion complexes with organic compounds and thereby increase the water solubility of the organic compound is known. In Cyclodextrins Increase Surface Tension and Critical Micelle Concentrations of Detergent Solutions by W.Saenger and A.Muller-Fahrnow, Agnew.Chem. Int. Ed. Egl. 27 (1988) No.3 at pages 393-394, the authors discuss the ability of the central hydrophobic cavity of the cyclodextrin compounds to accommodate the hydrophobic, aliphatic part of a detergent molecule having a diameter of about 5 Angstroms. Studies with such detergents showed that the cyclodextrins were capable of increasing the surface tension of the detergent molecule and shifting the critical micelle concentration of the detergent to a higher value, thus making the detergent more soluble in water. This was suggested as being beneficial in cases where micelles need to be destroyed or where surface tension needs to be increased, as for example to avoid foaming.

UK Patent application 2,189,245 A entitled Producing Modified Cyclodextrins, published on Oct.21, 1987, and assigned to American Maize-Products Company discloses a method for increasing the water solubility

of cyclodextrins. This method involves modification with alkylene carbonates and preferably ethylene carbonate to form hydroxyethyl ethers on the ring structure.

Applicants have found that because cyclodextrin compounds absorb onto or form complexes with hydrophobic species, they can be absorbed onto the hydrophobic moieties of associative thickeners. The absorption of cyclodextrin compounds onto the hydrophobic moieties of associative thickeners causes a suppression of the viscosity of an aqueous solution containing the associative thickener. It has been found that cyclodextrin compounds can be readily desorbed or decomplexed from the associative thickener by the addition of another material which has an affinity for the cyclodextrin.

Applicants have found that not only can the alpha, beta and gamma cyclodextrins be used effectively as transient viscosity suppressing agents for hydrophobic associative thickeners, but that modified cyclodextrins, such as for example those cyclodextrins produced by the process described in UK Patent application 2,189,245 A, which are more soluble in water than the unmodified cyclodextrin compounds can also be employed in this manner. In fact applicants have found it preferable to utilize hydroxyethyl--- or hydroxypropyl- cyclodextrins having a higher

degree of water solubility than the unmodified cyclodextrins for use with aqueous solutions containing high concentrations of associative thickener.

The least water soluble of the unmodified cyclodextrins is beta-cyclodextrin. The water solubility limit of beta cyclodextrin is about 2 grams per 100 grams of water. This limits the concentration of beta cyclodextrin which can be employed to suppress the viscosity of an aqueous solution containing an associative thickener. Since the viscosity of an aqueous solution containing an associative thickener increases with the concentration of the associative thickener solids, the solubility limit of the cyclodextrin determines the maximum amount of cyclodextrin which can be added to the solution without resulting in the formation of undesirable solids. If the maximum concentration of a viscosity suppressing additive needed to reduce the viscosity of an aqueous solution containing an associative thickener to a handleable viscosity, such as for example a viscosity of about 2,000 cps, exceeds the solubility limit of the additive in water, then the additive is not effective as a viscosity suppressant additive. In other words, the effectiveness of a cyclodextrin as a viscosity suppressing additive is a function of the solubility limit of the cyclodextrin and the solids content of the associative thickener in the aqueous solution. The higher the solids content of the associative

thickener the higher the viscosity of the aqueous solution containing it will be, and likewise the higher the concentration of the cyclodextrin which will be needed to be added to suppress the viscosity down to a handleable viscosity. This relationship between the solubility limit of the cyclodextrin and the viscosity of an aqueous solution containing an associative thickener is critical in the selection of an effective cyclodextrin for use as a viscosity suppressing additive. As described in more detail below, this relationship favors the selection of unmodified cyclodextrins other than beta cyclodextrin, and modified cyclodextrin additives having increased water solubility in cases where the aqueous solutions contains high concentrations of associative thickener solids.

Applicants have found that the use of beta-cyclodextrin and its ethoxylate and propoxlate derivatives are useful in latex paint formulation for achieving a variety of effects, such as for example: to permit the preparation and supply of a low viscosity, high solids solution of the thickener without the use of viscosity suppressing solvent; improving the ease of incorporating hydrophobically modified, associative thickeners, having marginal solubility in water, into aqueous systems; to reduce the viscosity drop of associative thickener containing formulations upon the addition of colorants or surfactants to the

formulation; to improve the efficiency of the associative thickener itself, thus reducing the thickener required to reach a given paint viscosity; to reduce foaming in a paint, with or without an associative thickener, which is especially desirable when the paint is to be applied by a roller; and to reduce the color development problems caused by surfactants in some formulations.

In aqueous solutions containing low concentrations of associative thickener solids, for example on the order of about 3 percent by weight, we have found that the unmodified cyclodextrins, including beta cyclodextrin, are effective viscosity suppressing additives, while in aqueous solutions containing high concentrations of associative thickener solids, for example on the order of greater than about 10 percent by weight, we have found the modified cyclodextrins, having increased water solubility on the order of about 50 grams per 100 grams water, are preferred.

As illustrated in the examples which follow we have found that handleable viscosities can be achieved with polyurethane type associative thickeners at low solids concentrations from about 3% to about 12 % by weight using from about 0.5 % to about 2% of a beta-cyclodextrin having a water solubility of 2 grams per 100 grams water. Modified cyclodextrins,

such as for example the hydroxyethyl-- or hydroxypropyl- cyclodextrins , can also be effectively used with low solids associative thickeners.

With high solids associative thickeners containing on the order of about 20% by weight of a urethane associative thickener, we found that only the modified cyclodextrins were effective viscosity suppressing additives since the concentrations which were required to be added exceeded the water solubility limits of the unmodified cyclodextrins. In the case of such high solids urethane associative thickeners we found that it was necessary to employ about 10% of the modified cyclodextrins to achieve handleable viscosities.

The ability to decomplex the cyclodextrin additive from the hydrophobic associative thickener is just as important as the ability of the cyclodextrin to absorb or complex with the associative thickener in the first instance. It is critical for the thickener to perform its intended viscosity increasing function in the aqueous system to which the associative thickener solution is added that the cyclodextrin becomes decomplexed or desorbed from the hydrophobic moieties on the associative thickener molecule. We have found that cyclodextrins are readily desorbed or decomplexed from hydrophobic associative thickeners simply by the addition of a material which has an affinity for the cyclodextrin. In this

regard we have found that conventional surface active agents commonly employed in aqueous coating systems, such as for example anionic surfactants like sodium lauryl sulfate and nonionic surfactants such as for example Igepal CO-660 (a 10 mole ethoxylate of nonyl phenol), and cationic surfactants, may be used to decomplex or desorb the cyclodextrin. Other water soluble organic solvents such as for example ethanol and Texanol^{*} may also be employed for this purpose but are not preferred. We have found that it is preferred to utilize about one mole of the decomplexing agent per mole of the cyclodextrin added to the associative thickener solution in order to achieve complete desorption or decomplexation. Both the complexation and decomplexation mechanisms are easily achieved by the addition of the reactants with mixing. No special purification or separation steps are required . In our experiments with certain latex paint formulations we have unexpectedly found that it is not necessary to add additional surfactant to cause this decomplexation process to occur; the formulation surfactants already present in the paint have been found to be sufficient. When the cyclodextrin- modified thickeners are added to the paint formulation at equal levels, based on the thickener component in the formulation, those modified with cyclodextrin have been shown to possess a slightly better efficiency (higher

* Trademark

equilibrated Krebs-Stormer viscosity) than those containing the unmodified thickener. Formulation surfactants in the paint tend to suppress the development of associative thickening. Therefore, the formation of the surfactant-cyclodextrin complex, which occurs as the thickener is activated, reduce the effective surfactant concentration in the formulation, thus increasing the equilibrated viscosity. Addition of further surfactants over a wide range of hydrophilic-hydrophobic balances (HLBs) and from 1 to 5 mole equivalents of surfactant to cyclodextrin causes a decrease in viscosity. Those thickeners modified with cyclodextrins, especially the propoxylate modified cyclodextrins, are less affected by the surfactant addition.

The viscosity stabilizing effect of the cyclodextrins can be further utilized by post adding the cyclodextrins to the associatively thickened formulation. As demonstrated by illustrative example 9 presented hereinafter, the viscosity loss which occurred upon the addition of predispersed colorant to the formulation was reduced by increasing levels of cyclodextrins. The data presented in example 9, clearly demonstrates the innate viscosity instability of this type of associative thickener can be reduced by the post-addition of cyclodextrins thus making the thickener less formulation sensitive.

One of the limitations in associative thickener chemistry is the latitude one has on the size of the hydrophobe relative to the hydrophilic backbone of the molecule. As the hydrophobe become larger, it become more associative and thus more efficient. However, a practical limitation is reached when the thickener no longer can incorporate into the aqueous phase of the paint. In current associative thickener technology, the incorporation of the thickener in many formulations is undesirably slow. We have demonstrated that we can improve the incorporation of the thickener. In the illustrative examples presented hereinafter we have demonstrated that the time required to incorporate the cyclodextrin modified compared with the unmodified thickener. To do this, the thickener was added to the formulation and the time required for the thickener to dissolve in the formulation was measured under similar stirring conditions for each of the thickeners. The results demonstrated that the cyclodextrins modified thickeners were incorporated in one fourth of the time required by the unmodified thickener.

The surfactant complexing effect of the cyclodextrins are also of benefit to the formulator for other properties than rheological modification.

Typically when formulating tinted paints, the composition of the formulation, specifically the surfactants, must be modified to maintain the stability of the colorant dispersion while not adversely affecting the dispersion of the other components. In some formulations, the paint components, such as the latex vehicle, bring an incompatible surfactant into the formulation. To correct for this, additional surfactants are added to the formulation to compatibilize the system. While effective in compatibilizing the system, these surfactants can contribute adverse water sensitivity and foaming characteristics to the formulation. In the illustrative examples , presented hereinafter, we have demonstrated that cyclodextrins are useful in improving the compatibility of a colorant without adding additional surfactants.

The surfactant complexing effect of the cyclodextrins are also of benefit to the formulator for other properties. Because of the high surfactant loading required to prepare many latex paint vehicles, foaming in the formulated paint must be combatted. Current technologies for foam reduction are limited in efficacy by the formulation and application problems that they can cause. The use of ethoxylated cyclodextrins, and presumably cyclodextrin itself or other derivatives, is able to reduce the foaming tendency of two formulations without the development of any

adverse phenomena such as surface defects.

The following examples illustrate the operation of the invention using conventional associative thickeners. These examples are intended merely to illustrate the invention and are not intended nor should they be interpreted as limiting the scope of the invention since modifications to the process illustrated are considered to be obvious to one of ordinary skill in the art.

Example 1: Low Solids

This example demonstrated the effectiveness of beta-cyclodextrin to suppress the viscosity of an aqueous solution of a polyurethane associative thickener (Rohm and Haas Company, QR-708) at a low solids content of 3% by weight (3 grams solid QR-708 in 97 grams water). The associative thickener aqueous solution was prepared as follows: differing quantities of Beta-cyclodextrin (American Maize Company) was then added to aliquots of the associative thickener solution (3g solid QR-708 in 97g H₂O) with mixing in a jar on a shaker for 4 hours and allowed to stand overnight. The viscosity of the solutions were measured using a Brookfield viscometer (spindle number 4) at 30 rpm. Table 1 shows the results of the addition of the beta-cyclodextrin to the associative thickener solutions.

Table 1

Sample	beta-cyclodextrin grams	viscosity cps
1	0	210
2	0.0009	210
3	0.0117	192
4	0.0512	196
5	0.1010	204
6	0.1996	177
7	0.3030	108
8	0.4016	35
9	0.5056	14
10	1.0077	7

The results show that the viscosity of the associative thickener solution steadily fell as the amount of cyclodextrin was increased.

Example 2: Restoration of viscosity: anionic and nonionic surfactants

Next we determined whether it was possible to restore the viscosity of aqueous solutions containing 3% QR-708 (3 grams solid QR-708 in 97 grams water) and 1 gram beta-cyclodextrin to the original viscosity level of the 3% QR-708 solution by adding sodium lauryl sulfate ("SLS", 28%). We measured the viscosity of the solution as in Example 1 as the amount of SLS was added. Table 2 shows the results.

Table 2

Sample	SLS grams	viscosity ,cps
11	0.01	10
12	0.09	10
13	0.47	48
14	0.89	191

The original viscosity of the solution was recovered upon the addition of 0.25 grams of SLS solids (0.89 grams of 28% SLS), which is equivalent to 1 mole of SLS per mole of beta-cyclodextrin added.

This experiment was repeated using a nonionic surfactant, Igepal CO-660. The results are shown in Table 3.

Table 3

Sample	Igepal CO-660, grams	viscosity, cps
15	.29	50
16	.58	725

This shows that the original viscosity was recovered upon the addition of 0.58 grams of the nonionic surfactant, which is equivalent to 1 mole per mole of beta-cyclodextrin.

EXAMPLE 3: Restoration of viscosity: cationic surfactants and organic solvents

To a solution of 3g of a 100% solids, QR -708 (3 grams solid QR-708 in 97 grams water) and 1g of beta-cyclodextrin (from American Maize) in 97g of DI water was added the following quantities of a cationic surfactant 18/25 (Ethoquad is the registered trade mark of Akzo Chemicals Inc. and is chemically methylpolyoxyethylene (15)octadecyl ammonium chloride). Table 4 show results.

Table 4

Sample	Cationic Surfactant 18/25	viscosity, cps	Spindle #
17 Comparative	0g	5	1
18	.23g	11	1
19	.45g	123	1
20	.68g	484	3
21	.91g	1,060	4

Viscosities were determined on a Brookfield viscometer at 30 rpm using the spindle number indicated above. This shows that the original viscosity was recovered upon the addition of 0.91g. of the cationic surfactant.

Further, the ability of organic solvent for recovering original viscosity was also examined using Texanol^{*} (2,2,4-trimethyl-3-hydroxypentyl acetate) and propylene glycol. The results are shown in Table 5.

Table 5

Sample	Texanol, grams	Propylene glycol, grams	viscosity, cps
22	0.10	- -	18
23	0.19	- -	299
24	---	.03	7
25	---	0.07	6
26	---	0.14	6
27	---	0.21	8

The results showed that the organic solvents were less effective than either of the surfactants for recovering original viscosity, and while
*
Texanol was useful, propylene glycol was not.

Example 4: High Solids

This example demonstrates the effectiveness of beta cyclodextrin as a viscosity suppressing additive for high solids urethane thickener solutions. A series of samples containing either 0 grams, 1.5 grams or 2 grams beta-cyclodextrin and varying concentrations of the urethane associative thickener (total solution weight is 100g) were prepared in accordance with example 1. Table 6 shows the viscosity of each of the solutions.

Table 6

Sample	Beta-cyclodextrin grams	QR-708 % solids	Viscosity cps	
28	Comparative	0	3	1,180
29	"	0	5	3,500
30	"	0	7.5	44,700
31	"	0	10	154,800
32	"	0	12.5	353,600
33	"	0	15	454,000
34	"	0	17.5	665,000
35	"	0	20	870,000
36	1.5	3	60	
37	1.5	5	70	
38	1.5	7.5	4,750	
39	1.5	10	4,750	
40	1.5	12.5	20,150	
41	1.5	15	40,000	
42	1.5	17.5	214,000	
43	1.5	20	478,000	
44	2.0	3	7	
45	2.0	5	12	
46	2.0	7.5	35	
47	2.0	10	1,050	
48	2.0	12.5	15,650	
49	2.0	15	27,800	
50	2.0	17.5	86,900	
51	2.0	20	240,800	

The results show that a viscosity of about 2000 cps can be achieved at around 10-12% QR-708 solids using 2 grams of the beta-cyclodextrin, while this viscosity can be achieved at 8% solids using 1.5 grams beta-cyclodextrin.

Example 5: Alpha- and Gamma Cyclodextrins

This example demonstrates the effectiveness of alpha cyclodextrin and gamma cyclodextrin as viscosity suppressing additives for urethane associative thickeners.

To solutions containing 3 grams QR-708 (100% solids) were added the materials shown in Tables 7 and 8 respectively. The samples were then capped and agitated for three hours and then put in a water bath at 25 degrees C. for 16 hours. The viscosity of each sample was then measured using a Brookfield viscometer at 30 rpm using the spindle # indicated.

Table 7**Alpha-Cyclodextrin**

Sample	Alpha-cyclodextrin grams	Deionized Water grams	Viscosity cps	Spindle #
52 Comparative	0	97.00	1,540	4
53	0.10	96.90	900	4
54	0.25	96.75	172	3
55	0.50	96.50	14	2
56	1.00	96.00	4	1

Table 8

Gamma Cyclodextrin

Sample	Gamma-cyclodextrin grams	Deionized Water	Viscosity cps	Spindle #
57Comparative	0	97.00	1,540	4
58	0.10	96.90	1,340	4
59	0.25	96.75	1,096	3
60	1.00	96.00	114	2

Example 6: Cyclodextrin Derivatives

This example illustrates the use of modified cyclodextrins as viscosity suppressing additives for both low solids and high solids urethane associative thickeners. The cyclodextrins used were ethoxylated (EO-CD) and propoxylated beta-cyclodextrins(PO-CD) obtained from American Maize Company. The solutions were prepared and the viscosities were determined using the procedure of example 1 (total solution weight was 100g). The results are shown in Table 9.

Table 9

Modified Cyclodextrins

Sample	Cyclodextrin Type, grams	QR-708 %solid	Viscosity cps
61Comparative	0 EO-CD	3	1,364
62	.1	3	1,436
63	.2	3	1,184
64	.5	3	584
65	1.0	3	6
66Comparative	0 EO-CD	20	313,600
67	2	20	298,400
68	4	20	181,600
69	5	20	135,200
70	6	20	36,400
71	7	20	20,400
72	8	20	2,984
73	10	20	684
74	2 PO-CD	20	528,000
75	4	20	133,200
76	6	20	9,600
77	8	20	760
78	10	20	460

Example 7: OTHER ASSOCIATIVE THICKENERS

This example demonstrates the utility of the cyclodextrin additives as viscosity suppressants for aqueous solutions containing other types of associative thickeners.

The thickeners used in this experiment were: Acrysol TT-935 (Rohm and Haas Company), a hydrophobically modified alkali soluble emulsion thickener, and a hydrophobically modified hydroxyethyl cellulose thickener (Natrosol Plus from Aqualon). A unmodified (non-hydrophobic) hydroxyethyl cellulose thickener was also evaluated. Each of these thickeners were formulated separately in aqueous solutions at various concentrations and the beta-cyclodextrin additive was added as described in example 1. The viscosities of the solutions were measured as in example 1 and the results are shown in Table 10.

* Trademark

Table 10

OTHER ASSOCIATIVE THICKENERS

Sample	Beta-cyclodextrin grams	Associative thickener grams and type	Viscosity cps
79Comparative	0	2.0 solid TT-935 *	411
80	0.25	" "	146
81	0.5	" "	99
82	0.75	" "	33
83	1.0	" "	21
84Comparative	0	3 Nat. Plus **	4,240
85	0.25	" "	1,380
86	0.50	" "	400
87	0.75	" "	221
88	1.0	" "	165
89Comparative	0	3 HEC ***	3,520
90	0.25	" "	4,680
91	0.50	" "	5,120
92	0.75	" "	4,720
93	1.0	" "	4,880

* (1% solution) in .8g of 50 wt% NaOH and 197.2g H₂O

** (1.5% solution) in 197g H₂O

*** (1.5% solution) in 197 g H₂O

The results show that beta-cyclodextrin can reduce the viscosity of these two hydrophobically modified thickeners, TT-935 and Natrosol Plus, but has no effect on the viscosity for the non-hydrophobic thickener, hydroxyethyl cellulose (HEC).

Example 8: Latex Paint

This example demonstrates the use of the cyclodextrin additives in aqueous latex paint formulations containing associative thickeners. The composition of the latex paint formulation used in this example is shown below in Table 11.

Table 11

Latex Paint Formulation #1

Material	Pounds
Propylene glycol	70.00
* Tamol SG-1 dispersant(35%)	12.00
* Foamaster VL antifoaming agent	1.00
Water	45.00
Titanium dioxide Pure-R-900	210.00
China Clay	88.00
Water	116.70
* Texanol	11.40
AC-64 acrylic binder	378.00
* Foamaster VL	3.00
Water	42.00
Thickener plus water	92.80
PVC= 29.81, Volume solids = 34.86	

Table 12

**Thickening Efficiency in Latex Paint
Surfactant Addition Effects
Thickener type**

	HEUR	BCD	E-BCD	P-BCD
	Control			
Thickener Demand (dry lbs/100 gal) (based upon thickener component)	2.27	2.27	2.27	2.27
Viscosity - KU equil	102	110	111	105
- ICI	0.8	0.8	0.8	0.8
<u>Surfactant Addition</u>				
Triton [*] X-45	Viscosity change (KU)			
1 mole equiv.	- 5	- 4	- 5	- 3
2	-11	- 2	- 1	- 2
5	-17	- 6	- 7	- 3
Triton [*] X-100	Viscosity change (KU)			
1 mole equiv.	- 9	- 6	- 4	- 6
2	-27	- 6	- 6	- 5
5	-35	-14	-13	-10
Triton [*] X-405	Viscosity change (KU)			
1 mole equiv.	-19	-11	- 8	- 5
2	-34	-15	-12	- 2
5	-39	-32	-26	- 8

The cyclodextrin modified thickeners were added to the paint formulation at equal levels based on the thickener component in the formulation. Those modified with cyclodextrins (BCD is beta cyclodextrin, E-BCD is ethoxylated beta cyclodextrin and P-BCD is propoxylated betacyclodextrin) demonstrated better efficiency (higher equilibrated Krebs-Stormer viscosity) than the unmodified thickener (control, QR-708 is a hydrophobically modified ethoxylated urethane rheology modifier). Addition of further surfactants (ethoxylated octyl phenols -Triton^{*} X-45(5 EO units), X-100(9.5 EO units) and X-405(40 EO units))over a wide range of HLBs and from 1 to 5 mole equivalents of surfactant to cyclodextrin containing formulations caused decreases in viscosity.

Example 9 : Latex Paint : Post addition of cyclodextrins

This example demonstrated that the viscosity stabilizing effect of the cyclodextrin can be further utilized by the post addition of cyclodextrins to an associatively thickened paint formulation.

The latex paint used in this example had the composition shown in Table 13.

Table 13

Latex Paint Formulation #2

Material	Amount,pounds
Water	106.7
* Tamol 731(25%) dispersant	11.5
Propylene glycol	25.0
* Patcote 801 (defoamer)	2.0
Titanium dioxide-Pure R-900	250.0
* Optiwhite (China clay)	100.0
* Attagel 50(Attapulgate clay)	5.0
 Polymeric Binder AC-64	 350.00
* Texanol	10.60
* Patcote 801	4.00
 Thickener plus water	 234.70

PVC= 36.8, Volume solids=35.86

The latex paint formulation #2 was thickened to a viscosity of 110 Krebs Units with a hydrophobically modified ethoxylated urethane rheology modifier. To the thickened paint samples was post-added an equivalent of from 0 to 10 pounds of cyclodextrin per 100 gallons of the paint. After this each paint was tinted to an equivalent of 2 fluid ounces of predispersed lampblack colorant per gallon of paint. After stirring, the Krebs-Stormer viscosity of each paint sample was again measured. The viscosity difference between the initial viscosity and the viscosity after tinting was used as a measure of stability. Table 14 presents the results of this evaluation.

Table 14

Viscosity Stability Upon Colorant Addition

<u>Additive Level (lbs / 100 gal)</u>	<u>Viscosity Change (KU)</u>
0 lbs beta-CD	-34
1	-27
3	-12
5	- 3
7	+ 4
10	+ 4
0 lbs beta-CD ethoxylate	-34
1	-25
3	-14
5	- 3
7	+ 4
10	+ 8
0 lbs beta-CD propoxylate	-34
1	-25
3	- 8
5	+ 1
7	+ 4
10	+ 5

Example 10: Time to incorporate associative thickener

This example demonstrates the ability of the cyclodextrins to reduce the time required for the incorporation of associative thickeners in a latex paint formulation. The associative thickener was added to latex paint formulation #1, and stirred. The time required for the thickener to dissolve in the paint was measured. The results are shown in Table 15.

Table 15**Rate of Thickener Incorporation**

Thickener	Time to incorporate (min.)
HEUR (hydrophobically modified ethoxylated urethane rehelogy modifier-control)	120
Beta-cyclodextrin	29
Ethoxylated-beta cyclodextrin	27
Propoxylayed-beta-cyclodextrin	29

Example 11: Compatibility of colorant

A tint base formulation (Paint formulation #3: Table 16) was prepared with and without additional colorant stabilizing surfactants. To those paints formulated without the surfactants we added an equivalent of 0 to 10 lbs of ethoxylated cyclodextrin per 100 gallons of paint. After equilibration, the paints were cast on a Leneta WB sealed white chart using a 3 mil Bird applicator. The paint films were allowed to dry at 77° F and 50% relative humidity for 4 days. After drying was complete, approximately 10 grams of the same paint was cast on 3" band of each chart by brush and brushing was continued to dryness to provide significant shear to the paint being applied. After an overnight dry at 77° F and 50% relative humidity, the color acceptance of the paints were evaluated by measuring the difference in Y-reflectance of the brush vs. Bird cast films using a spherically integrating reflectometer. If the colorant and other components of the paints are properly dispersed, there would be no shear dependent change in the Y-reflectance of the film. While perfect color acceptance was not achieved, it is clear from the data that the use of an equivalent of 5 lbs of the ethoxylated cyclodextrins per 100 gallons yielded an improvement equal to the either or both of the surfactants listed in the formulation. While degree of color acceptance

problem in this example may be barely significant to human perception, the trend for improvement up to the 5 lbs level was clear when so measured .

Table 16

Paint Formulation #3

Material	Amount, pounds
The following were charged to the tank:	
* Tamol 850 dispersant (30%)	9.0
Water	2.0
Propylene glycol	60.0
Antifoamer	0.5

The following were added with low speed mixing:

High gloss rutile titanium dioxide	225.0
Barytes (barium sulfate)	40.0

The above was then ground in a high-speed mill (Cowles 3800-4500 feet per minute) for 10-15 minutes, and was then let down with the following at low speed mixing

Propylene glycol	95.5
Polymeric Binder Rhoplex [*] AC-490(46.5%)	526.0
[*] Acrysol G-110 Acrylic thickener	10.3
Mineral spirits	1.0
Water	68.7
Butyl Cellosolve	24.5
[*] Triton N-57 nonyl phenol ethoxylate	either 0.0 or 4.0
[*] Triton X-207 alkylaryl polyether alcohol	either 0.0 or 4.0
Tint : predispersed red iron oxide	4 ounces/100 gallons
PVC= 23.3%, Volume solids= 33.0%, gloss (60 degrees)=40-50	

Table 17

**Color Acceptance Modification with
beta-Cyclodextrin Ethoxylate**

Added Surfactant for Color Acceptance	Ethoxylated CD (lbs/100gal)	Y-Reflectance Difference (upon shear)
4lbs Triton* N-57 and 4lbs Triton* X-207	0	0.51
	1	0.43
	3	0.52
	5	0.56
	10	0.49
4lbs Triton* N-57	0	0.33
	1	0.32
	3	0.40
	5	0.35
	10	0.50
4lbs Triton* X-207	0	0.36
	1	0.36
	5	0.51
	10	0.63
	No added surfactant	0
1		0.42
3		0.36
5		0.32
10		0.58

Example 12: Reduction in Foaming in Latex Paint

This example demonstrates the use of cyclodextrins to reduce foaming in latex paints. The latex paint formulation used in this example is shown in Table 18 as Paint Formulation #4.

Table 18**Paint Formulation #4**

<u>Material</u>	<u>Pounds</u>
Methyl Carbitol *	39.0
Acrylic latex, Rhoplex HG-74 (42.5%)	598.5
Texanol *	37.0
Dowicil 75 premix	1.0
Water	5.0
Ammonium hydroxide (28%)	2.0
Water *	40.0
Defoamer, Foamaster AP	4.2
Carbon Black, Harshaw W-7012	25.0
Acrylic Thickener, Acrysol* RM-5 (30%)	22.8
Water premix	32.2
Ammonium hydroxide (28%)	2.2
Water	46.9

To test this formulation, the equivalent to 0 to 10 lbs of ethoxylated betacyclodextrin per 100 gallons of paint was added to the paint. After equilibration overnight, the paints were applied to a seal Leneta 12-H-BW chart using a 3", 3/8" nap synthetic fiber roller. The paint films were allowed to dry under ambient conditions. Surface defects in the film were rated by determining the frequency of defect on a 2 cm square area. The results in Table 19 show that at levels of 5 lbs/100 gallons of the ethoxylated cyclodextrin and higher, foaming defects were eliminated.

Table 19

Surface Defects - Roller Foam Test
Addition of beta-cyclodextrin ethoxylated

Additive Level CD-ethoxylate (lbs/100gal)	Foaming (Surface Defects / 2 cm sq.)
0	5
1	2
3	1
5	0
10	0

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for eliminating the need for organic solvents for hydrophobic associative thickeners useful for thickening aqueous systems comprising:
complexing said thickener with an effective amount of a cyclodextrin compound,
adding an effective amount of said complexed thickener to said aqueous system,
and
decomplexing said cyclodextrin compound from said thickener with an effective amount of a compound capable of complexing with the cyclodextrin compound.
2. The method of claim 1 wherein said cyclodextrin compound is selected from the group consisting of alpha, beta and gamma cyclodextrin and ethoxylated and propoxylated cyclodextrins.
3. The method of claim 1 wherein said compound capable of complexing with the cyclodextrin compound is an anionic, nonionic or cationic surfactant.
4. The method of claim 3 wherein said surfactant is added to said aqueous system at a concentration of about one mole per mole of said cyclodextrin compound.
5. The method of claim 1 wherein said hydrophobic thickener is selected from the group consisting of hydrophobically modified alkali soluble emulsions, hydrophobically modified hydroxethyl cellulose, and hydrophobically modified polyacrylamides.

6. The method of claim 1 wherein said effective amount of said cyclodextrin compound used to complex with said thickener reduces the viscosity of the thickener to a handleable viscosity but is not greater than the water solubility of said cyclodextrin compound.
7. A method for reversibly reducing the viscosity of an aqueous solution containing a hydrophobic associative thickener comprising reducing the viscosity of said aqueous solution by adding to said solution an effective amount of a cyclodextrin compound and increasing the viscosity of said aqueous solution containing said cyclodextrin compound by adding to said solution at least one mole, per mole of said cyclodextrin compound, of a compound capable of complexing with the cyclodextrin compound.
8. A method of using a cyclodextrin compound for reducing the viscosity of aqueous solutions containing hydrophobic associative thickeners comprising adding an effective amount of said cyclodextrin compound to said aqueous solution containing said hydrophobic associative thickener.
9. A method of improving the incorporation of a hydrophobically modified associative thickener into an aqueous formulation comprising adding to said formulation an effective amount of a cyclodextrin compound.

10. A method of reducing the loss of viscosity of an aqueous system containing a hydrophobic associative thickener and a colorant comprising adding to said aqueous system an effective amount of a cyclodextrin compound.
11. A method for improving the efficiency of hydrophobic associative thickeners in aqueous system comprising adding to said system an effective amount of a cyclodextrin compound.
12. A method for reducing the color development problems associated with surfactants in aqueous paint formulations comprising a hydrophobic associative thickener, the method comprising adding an effective amount of a cyclodextrin compound to said paint formulation.
13. A method for reducing foaming in a latex paint comprising adding an effective amount of a cyclodextrin compound to said latex paint.