



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2611123 C 2013/10/08

(11)(21) **2 611 123**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

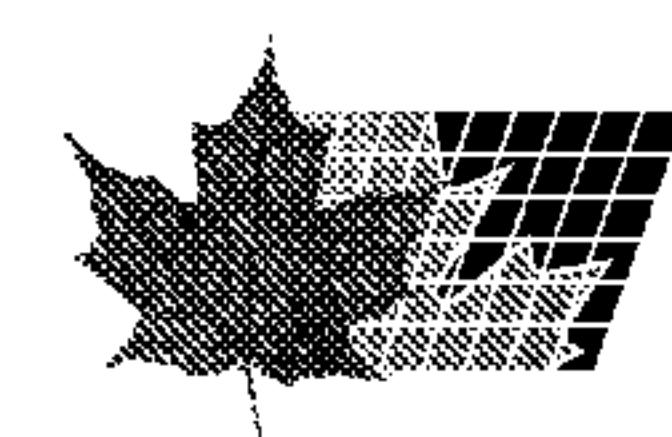
(86) Date de dépôt PCT/PCT Filing Date: 2006/05/29
(87) Date publication PCT/PCT Publication Date: 2006/12/07
(45) Date de délivrance/Issue Date: 2013/10/08
(85) Entrée phase nationale/National Entry: 2007/11/29
(86) N° demande PCT/PCT Application No.: EP 2006/062649
(87) N° publication PCT/PCT Publication No.: 2006/128836
(30) Priorité/Priority: 2005/06/02 (US60/686,779)

(51) Cl.Int./Int.Cl. *A01N 25/04* (2006.01),
A01N 25/14 (2006.01), *A01N 25/30* (2006.01),
A01N 43/70 (2006.01)
(72) Inventeur/Inventor:
ALEXANDER, MARK, US
(73) Propriétaire/Owner:
AKZO NOBEL N.V., NL
(74) Agent: NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

(54) Titre : MELANGES SYNERGIQUES DE SULFONATES DE CONDENSES D'(ALKYL) NAPHTALENE
FORMALDEHYDE ET DE LIGNOSULFONATES UTILES DANS DES FORMULATIONS AGROCHIMIQUES
(54) Title: SYNERGISTIC BLENDS OF (ALKYL) NAPHTHALENE FORMALDEHYDE CONDENSATE SULFONATES AND
LIGNOSULFONATES USEFUL IN AGROCHEMICAL FORMULATIONS

(57) Abrégé/Abstract:

The invention generally relates to a synergistic co-spray dried blend of (alkyl) naphthalene formaldehyde condensate sulfonates and lignosulfonates. This co-spray dried blend is useful as a dispersant in useful in agrochemical formulations.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
7 December 2006 (07.12.2006)

PCT

(10) International Publication Number
WO 2006/128836 A3

(51) International Patent Classification:

A01N 25/04 (2006.01) *A01N 25/30* (2006.01)
A01N 25/14 (2006.01) *A01N 43/70* (2006.01)

(21) International Application Number:

PCT/EP2006/062649

(22) International Filing Date: 29 May 2006 (29.05.2006)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/686,779 2 June 2005 (02.06.2005) US

(71) Applicant (for all designated States except US): **AKZO NOBEL N.V. [NL/NL]**; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ALEXANDER, Mark** [US/US]; 424 Avalon Gardens Drive, Nanuet, New York 10954 (US).(74) Agent: **SCHALKWIJK, Pieter Cornelis**; Akzo Nobel N.V., Intellectual Property Department (aip), P.o. Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:

10 May 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/128836 A3

(54) Title: SYNERGISTIC BLENDS OF (ALKYL) NAPHTHALENE FORMALDEHYDE CONDENSATE SULFONATES AND LIGNOSULFONATES USEFUL IN AGROCHEMICAL FORMULATIONS

(57) Abstract: The invention generally relates to a synergistic co-spray dried blend of (alkyl) naphthalene formaldehyde condensate sulfonates and lignosulfonates. This co-spray dried blend is useful as a dispersant in useful in agrochemical formulations.

SYNERGISTIC BLENDS OF (ALKYL) NAPHTHALENE FORMALDEHYDE
CONDENSATE SULFONATES AND LIGNOSULFONATES USEFUL IN
AGROCHEMICAL FORMULATIONS

5 Field of the Invention

The present invention generally relates to a synergistic blend of (alkyl) naphthalene formaldehyde condensate sulfonates and lignosulfonates useful in agrochemical formulations.

10 Background of the Invention

Lignosulfonates and naphthalene condensate sulfonates are both used as dispersants in agricultural formulations, specifically suspension concentrates, suspoemulsions, water dispersible granules and wettable powders. Typically they are used alone in a formulation, but there are instances where they are used together in 15 order to improve the physical stability and/or dilution performance of the finished product. When used together, the manufacturer will combine the individual liquids or powders into the formulation during manufacturing.

20 The present inventors have discovered an improved blend of lignosulfonates and naphthalene condensate sulfonates. More particularly, it has been discovered that the performance of lignin sulfonates plus naphthalene condensate sulfonates is increased when solutions of the two are blended and co-spray dried instead of blended together as individual powders, or added as individual solutions to the formulated product.

25

Summary of the Invention

30 The invention generally relates to a synergistic blend of (alkyl) naphthalene formaldehyde condensate sulfonates and lignosulfonates useful in agrochemical formulations. More particularly, the invention relates to a synergistic co-spray dried blend lignosulfonates and naphthalene condensate sulfonates.

35 In another aspect the invention relates to a process for preparing an improved dispersing agent composition in the form of a free flowing powder, said process comprising a step of co-drying a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate, the process comprising the sub-steps of blending an aqueous mixture of a) and an aqueous mixture of b), in order to

obtain a blended aqueous mixture of components a) and b), followed by drying said blended aqueous mixture in order to obtain the improved dispersing agent composition in the form of a free-flowing powder.

5 In still another aspect the invention relates to a suspension concentrate that comprises a biologically active agent, for example an insecticide, herbicide, fungicide, plant growth regulator, or mixtures thereof; and a dispersing effective amount of at least one dispersing agent of the invention.

10 Detailed Description of the Invention
The present invention relates to an improved dispersing agent composition useful in the agricultural industry. The dispersing agent composition of the present invention comprises a free-flowing powder of a blend of a) at least one lignin sulfonate, and b) at least one naphthalene condensate sulfonate. The free flowing powder of the

15 invention is obtained by blending an aqueous solution of component a) and b), followed by a drying step. Drying can be accomplished by various means, including evaporation, freeze-drying, spray drying and the like. In one embodiment, the drying is accomplished in a (co-) spray drying step.

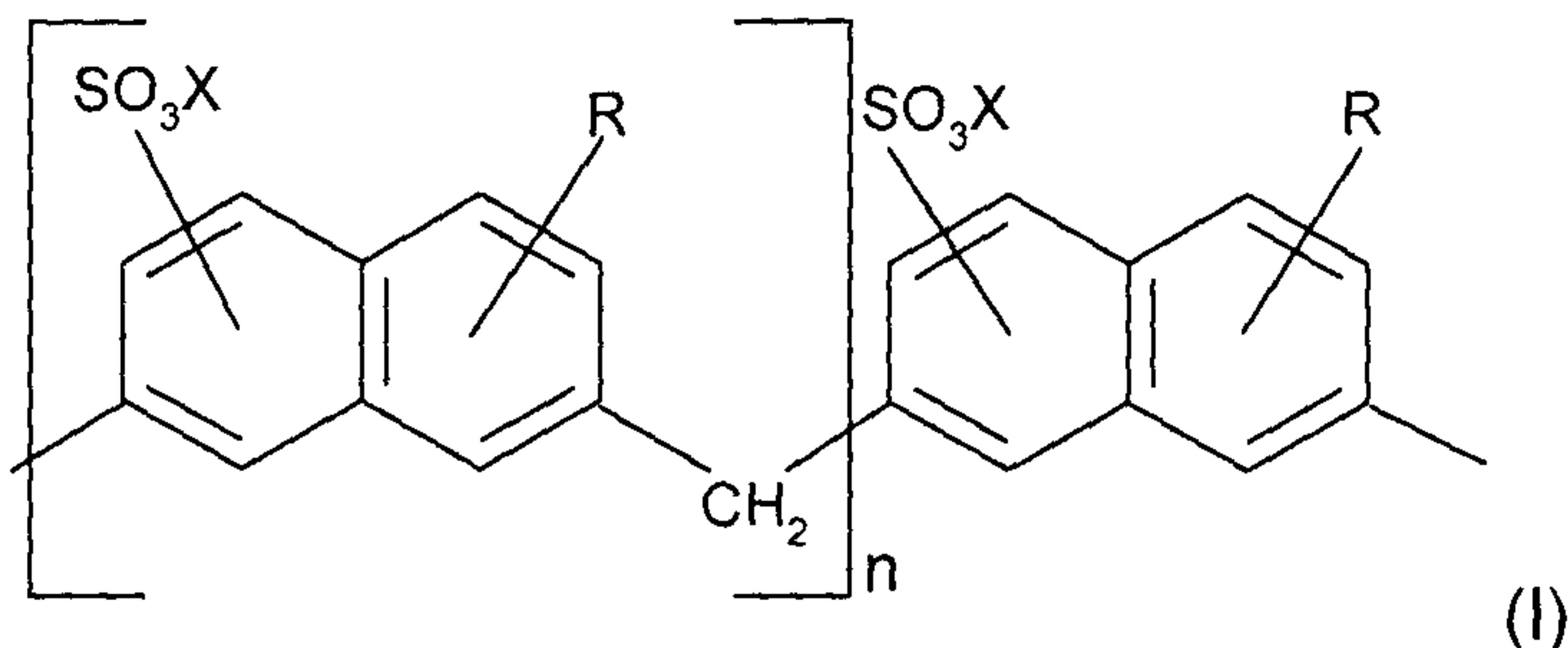
20 The present inventors have found that the performance of lignin sulfonates plus naphthalene condensate sulfonates is increased when solutions of the two are blended and dried, such as by spray-drying, instead of blended together as individual dry powders, or added as individual solutions to the formulated product.

25 Exemplary components a) are water-soluble salts of lignin sulfonate, e.g., the sodium, potassium, magnesium, calcium or ammonium salts of lignin sulfonate are preferably employed as component a) of the synergistic blend disclosed herein. The sodium salt of lignin sulfonate is preferred for use herein. Any commercially available lignin sulfonate salt which does not contain added surfactant, may be conveniently

30 employed herein. Commercially available lignin sulfonate emulsifiers include, but are not limited to: Reax^{RTM}, LTS, LTK and LTM, respectively, the potassium, magnesium and sodium salts of lignosulfonate (50% aqueous solutions), Scott Paper Co., Forest Chemical Products; Marasperse CR^{RTM} and Marasperse CBOS-3^{RTM}, sodium lignosulfonate, and Marasperse C21^{RTM}, calcium sulfonate, Reed Lignin Co., Polyfon

35 O^{RTM}, Polyfon T^{RTM}, Reax 88B^{RTM}, Reax 85B^{RTM}, sodium salts of lignin sulfonate, Westvaco Polychemicals.

Component b) is an alkyl naphthalene formaldehyde condensate sulfonate of the formula (I):



5 wherein each R is independently hydrogen, a C₁₋₃₀ straight or branched chain alkyl or alkenyl group, preferably a C₁₋₄ alkyl group; and each X is independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, a mono-, di-, or tri- C₁₋₄ alkyl ammonium, or a mono-, di- or tri- C₁₋₄ hydroxyalkyl ammonium moiety. In the above formula I, it is understood that the R groups can be present in any position on the
10 naphthalene nucleus. The n groups show the repetition of the monomer units. In most embodiments, each n is on average from 1-25.

The alkyl naphthalene condensate sulfonates of formula I are preferably manufactured by the process of U.S. Patent No. 5,110,981 to Milstein. As stated in
15 this patent, the alkyl naphthalene condensate sulfonates are usually obtained in the form of mixtures, containing both mono- and di-alkyl sulfonates, as well as small quantities of unreacted naphthalene and/or unsulfonated alkyl naphthalenes which will not interfere with their use in the practice of the present invention.

20 In general, components a) and b) are mixed together at 100% active concentrations in the following ratio 5:95 to 95:5, in another embodiment 10:90 to 90:10, in another embodiment 15:85 to 85:15, in another embodiment 25:75 to 75:25 and in still another embodiment of 50:50. Thereafter, aqueous solutions of each are prepared for use in preparing the free flowing powder of the invention.

Each of components a) and b) are typically obtained as 45% solids solutions from the respective synthesis routes. Once obtained, aqueous solutions of a) and b) are mixed together to form an aqueous blend of a) and b). Alternatively, a dry, or semi-dry powders of each of components a) and b) can be utilized.

5 Said (semi)dry powders could be blended either before and/or after the addition of water, with the objective of obtaining an aqueous blend of a) and b).

The quantity of solution a) and b) are blended together to give the desired ratio, such as 15:85 and 85:15, based on the percent solids present in solution a) and

10 b). Either solution a) or b) would be charged into the appropriate tank and heated to a target temperature to facilitate homogeneity, typically between 50°C and 70°C. Once the target temperature has been achieved the other solution is added to the tank. That mixture is mixed until homogenous. Homogeneity should be verified via analysis before the solution is dried.

15

Thereafter, the aqueous blend of a) and b) is dried in order to get the dry free-flowing powder of the invention. In one embodiment, the liquid blend is dried using a Co-current type spray drier. Suitably it is a top fed, atomized spray drier. The inlet temperature on the drier ranges from 300°F to 500°F and the outlet

20 temperature ranges between 200°F and 270°F. The liquid is fed into the drier at a rate of between 10 and 20 gallons per minute.

The dry blends of the alkyl naphthalene condensate sulfonates and lignosulfonates are used as dispersants for wettable powders, water dispersible

25 granules, suspension concentrates and suspoemulsions. Generally the blend is used with either non-ionic or an-ionic surfactant(s) acting as wetting agent or formulation stabilizer. The blends are used in suspension concentrates and suspoemulsions at a concentration range of 1.0 to 20%wt of the formulation, preferably 1.0 to 12.5%wt. Ideal embodiments utilize between 2.0 and 7.5%wt.

30 In water dispersible granules and wettable powders, the use rate can range between 1.0 and 25%wt, preferably 2.0 to 15%wt but most desired between 2.5 and 10%wt.

The dry blends of the present invention can be used to disperse any, and all, biologicallyactive substances, for example, insecticides, herbicides, fungicides and plant growth regulators that have a water solubility of less than 1000 ppm and a melting point of greater than 50⁰C. The most preferred properties would be a water 5 solubility of less than 400 ppm and a glass transition temperature of 40⁰C or higher.

The invention will now be illustrated by the following non-limiting example.

Example:

10 Two Atrazine suspension concentrates were produced; one using MorwetTM D-425 plus lignosulfonate, made by dry blending the two dry products, and the second used a MorwetTM + lignin powder wherein aqueous solutions of each were prepared, mixed, and co-spray dried. The following recipe was used to make the suspension concentrates:

15

Atrazine - 43.0%wt

Dispersant blend - 2.5%wt

Water - 54.5%wt

20 The technical was dry milled to an average particle size of 5 microns, so the finished suspension concentrates were not wet milled. The dispersant blend was added to the water and mixed until homogenous. The technical was then added and dispersed using high shear. Shearing continued until all of the technical was wetted and dispersed. The suspensibility of the suspension concentrates was measured using 25 CIPAC method MT161.

The suspensibility of the two suspension concentrates was measured, and the results were:

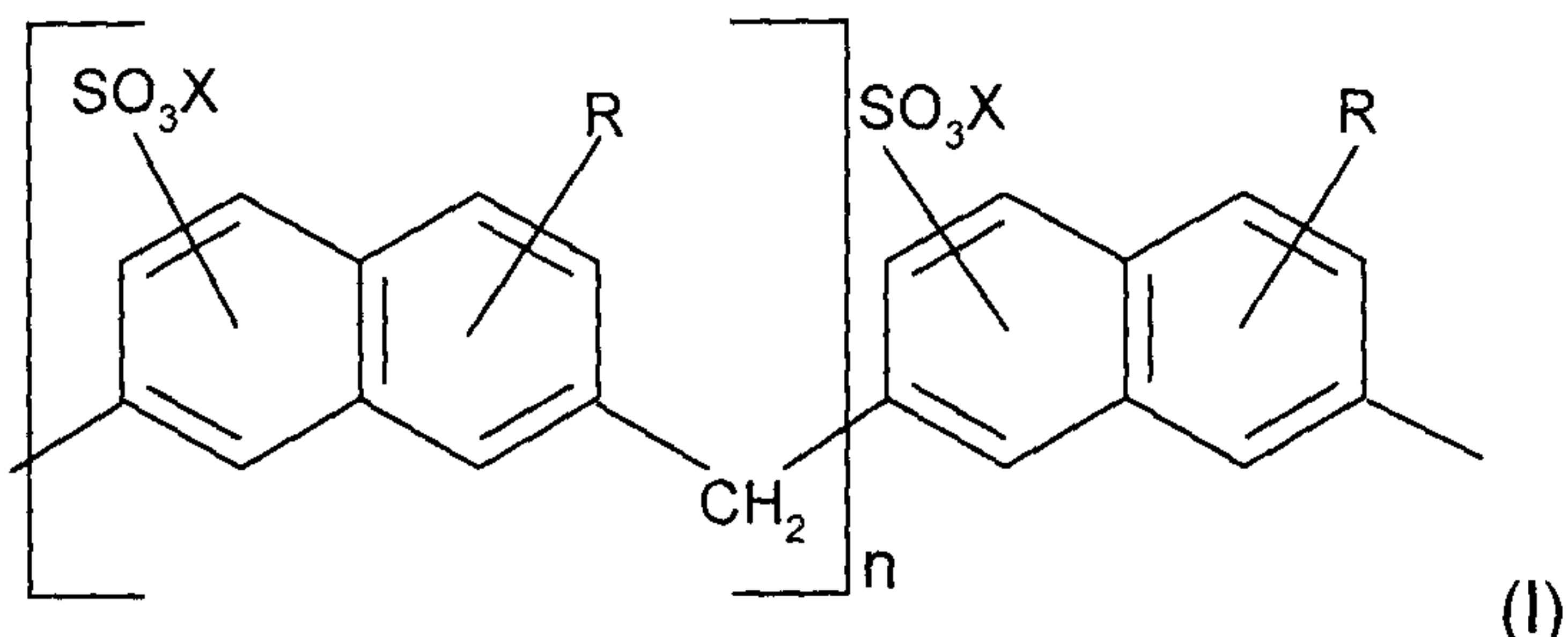
<u>Dispersant</u>	<u>345 ppm water % suspensibility</u>	<u>1000 ppm water % suspensibility</u>
Calcium lignin : D-425 (mix)	59.8	14.9
Calcium lignin : D-425 (codry)	83.4	49.8

5

The suspensibility of the suspension concentrate that contained the co-dried dispersant blend of the invention was substantially higher in 345ppm and 1000ppm water when compared to the suspension that contained the dry blend of dispersants according to the prior art. This result is both surprising and 10 unexpected.

CLAIMS

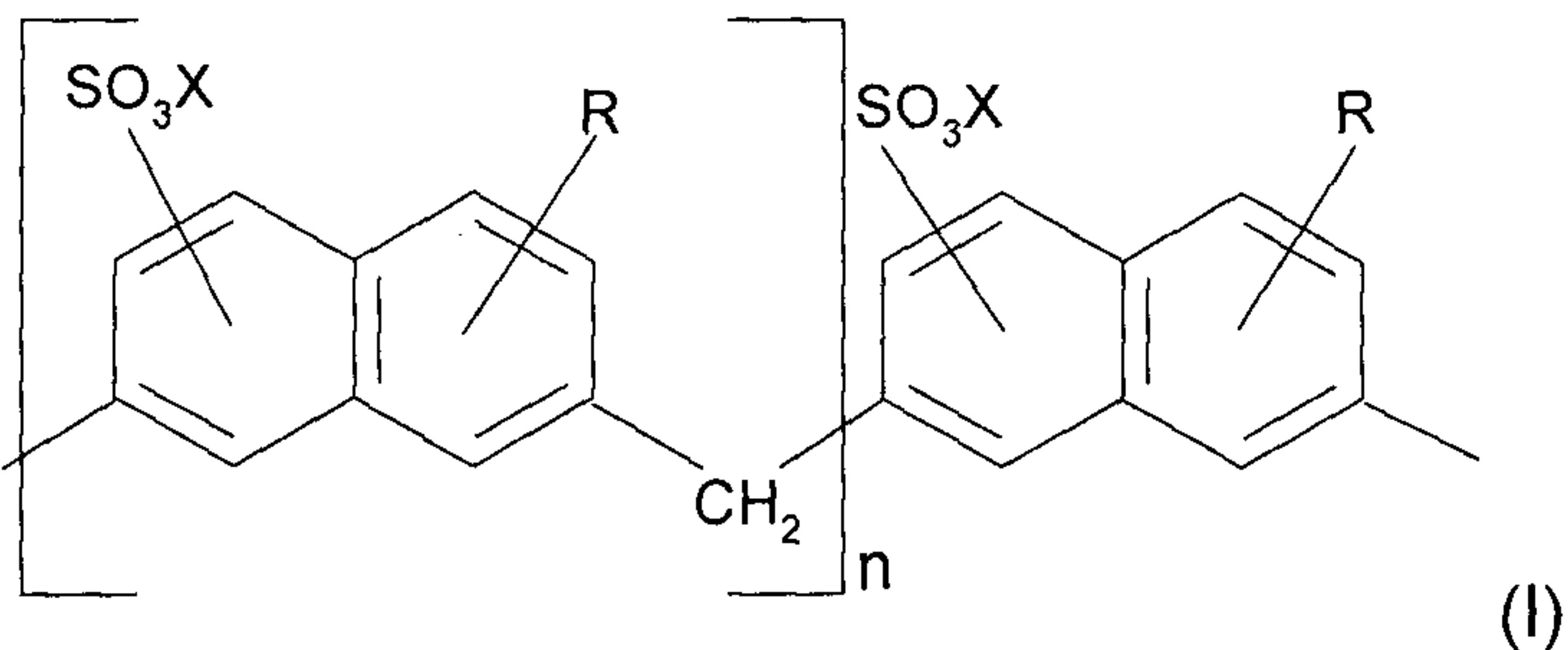
1. A process for preparing an improved dispersing agent composition in the form of a free flowing powder, said process comprising a step of co-drying
 - a) at least one lignin sulfonate, and
 - b) at least one naphthalene formaldehyde condensate sulfonate,
 said process comprising the sub-steps of blending an aqueous mixture of a) and an aqueous mixture of b), in order to obtain a blended aqueous mixture of components a) and b), followed by drying said blended aqueous mixture in order to obtain said improved dispersing agent composition in the form of a free-flowing powder.
2. The process of claim 1, wherein said at least one lignin sulfonate is a water-soluble salt of lignin sulfonate.
3. The process of claim 2, wherein said water-soluble salt of lignin sulfonate is the sodium, potassium, magnesium, calcium or ammonium salt of lignin sulfonate.
4. The process of any one of claims 1 to 3, wherein said at least one naphthalene condensate formaldehyde sulfonate is of the formula (I):



wherein each R is independently hydrogen, a C₁₋₃₀ straight or branched chain alkyl, or alkenyl group; each X is independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, a mono-, di-, or tri- C₁₋₄ alkyl ammonium, or a mono-, di- or tri- C₁₋₄ hydroxyalkyl ammonium moiety, and n is an integer of from 1-25.

5. The process of claim 4, wherein each R is independently a C₁₋₄ alkyl group.

6. The process of any one of claims 1 to 5, wherein the ratio of component a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate is in the range of from about 5:95 to 95:5 at 100% actives concentration.
7. The process of claim 6, wherein the ratio of component a) to component b) is in the range of from about 10:90 to 90:10 at 100% actives concentration.
8. The process of claim 7, wherein the ratio of component a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate is in the range of from about 25:75 to 75:25 at 100% actives concentration.
9. An improved dispersing agent composition in the form of a free flowing powder, wherein said composition comprises a dried blend of a) at least one lignin sulfonate, and b) at least one naphthalene condensate sulfonate, wherein said dispersing agent composition has a % suspensibility of at least 83% based on a 43 wt% Atrazine suspension concentrate containing 345 ppm water, measured according to CIPAC method MT161, and wherein said dried blend is obtained by blending an aqueous mixture of a) and an aqueous mixture of b) to obtain a blended aqueous mixture of components a) and b) followed by drying said blended aqueous mixture.
10. The composition of claim 9, wherein said at least one lignin sulfonate is a water-soluble salt of lignin sulfonate.
11. The composition of claim 10, wherein said water-soluble salt of lignin sulfonate is the sodium, potassium, magnesium, calcium or ammonium salt of lignin sulfonate.
12. The composition of any one of claims 9 to 11, wherein said at least one naphthalene condensate sulfonate is an alkyl naphthalene condensate sulfonate of the formula (I):



wherein each R is independently hydrogen, a C₁₋₃₀ straight or branched chain alkyl, or alkenyl group; each X is independently hydrogen, an alkali metal, an alkaline earth metal, ammonium, a mono-, di-, or tri- C₁₋₄ alkyl ammonium, or a mono-, di- or tri- C₁₋₄ hydroxyalkyl ammonium moiety, and n is from 1-25.

13. The composition of claim 12, wherein each R is independently a C₁₋₄ alkyl group.
14. The composition of any one of claims 9 to 13, wherein the ratio of component a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate is in the range of from about 5:95 to 95:5 at 100% actives concentration.
15. The composition of claim 14, wherein the ratio of component a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate is in the range of from about 10:90 to 90:10 at 100% actives concentration.
16. The composition of claim 15, wherein the ratio of component a) at least one lignin sulfonate, and b) at least one naphthalene formaldehyde condensate sulfonate is in the range of from about 25:75 to 75:25 at 100% actives concentration.
17. A suspension concentrate that comprises an insecticide, herbicide, fungicide, plant growth regulator, or mixtures thereof; and a dispersing effective amount of at least one dispersing agent according to any one of claims 9 to 16.
18. The concentrate of claim 17, wherein said dispersing agent is present in an amount of from about 1.0 to 20%wt based on the weight of the concentrate.
19. The concentrate of claim 18, wherein said dispersing agent is present in an amount of from about 2.0 to 7.5%wt based on the weight of the concentrate.