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Patente de Invención: FORMULACIÓN SÓLIDA DE MEZCLAS FUNGICIDAS

Atentamente se dirige a usted **JAIME EDUARDO DELGADO VILLEGAS**, Abogado, mayor y vecino de Bogotá D.C., e identificado como aparece al pie de mi firma para manifestarle lo siguiente:

1. Como apoderado de la sociedad BAYER CROPSCIENCE AKTIENGESELLSCHAFT, domiciliado en Monheim, Alemania, solicité ante su Digno Despacho el registro de la Patente de Invención que se enuncia en la referencia.
2. Fui requerido por su Despacho mediante Oficio No. 11775 del 4 de julio de 2012.
3. Como es de conocimiento de su Digno Despacho, para dar cumplimiento al oficio No. 11775, dentro de oportunidad legal el día 3 de octubre de 2012, solicite la suspensión del trámite, debido a que mis clientes la sociedad BAYER CROPSCIENCE AKTIENGESELLSCHAFT, no habían obtenido dichos documentos.

Por lo anteriormente enunciado y encontrándome dentro de oportunidad legal, me permito adjuntar lo siguiente:

- HUMPHERY S T ET AL. "Agrochemical formulations using natural lignin products Agrochemical formulations using natural lignin products." Chemistry and technology of agrochemical formulations. 1998, KLUWER ACADEMIC PUBLISHER, Páginas 158 a 178.
- DELLI H T ET AL. "The physical chemistry of WDGs: Porosity and surfactant dissolution as a function of dispersant molecular weight". ASTM special technical publication, 2001, Vol: STP 1400, Páginas 141 a 151.

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- WINOWISKI T ET AL. "Improved efficacy of lignosulfonate dispersants through a novel combination." ASTM special technical publication, 2003, Vol: STP 1430, páginas 66 a 74.

Los documentos que se mencionan con anterioridad se encuentran en su idioma original, debido a que en el presente Oficio el examinador no requiere de forma explícita las traducciones al español de los documentos solicitados.

En caso de que sea necesario presentar la traducción a la documentación adjunta, solicito comedidamente a su Despacho requerir con posterioridad mediante un Oficio explícito, indicando qué documentos deben ser traducidos -sólo en el caso de que sea necesario-.

Con la documentación adjunta, doy cumplimiento a lo requerido por su Digno Despacho, por lo que comedidamente solicito se continúe con el trámite normal de registro de la patente de invención enunciada en la referencia.

Atentamente,

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6 Agrochemical formulations using natural lignin products

S. T. HUMPHREY

6.1 Introduction

Lignosulphonates have a long association with the formulation of agrochemical products. They are to be found in many traditional formulation types, but are also considered an invaluable resource for formulation researchers looking at new and novel agrochemical delivery systems. For the purpose of this article the term lignosulphonates will be taken to embrace those products derived from both sulphite and kraft pulping processes.

6.1.1 Lignosulphonates: some basic information

Commercial development of lignosulphonates and their specialized derivatives has resulted in what was once a waste product becoming an important part of the speciality chemicals market, and lignin must be regarded as a valuable natural resource. The raw material for the cellulose industry – wood – consists mainly of three types of chemical compounds: cellulose, hemicellulose and lignin.

A number of models have been proposed to describe the structure of the lignin, but Freudenberg's 1964 formula (Figure 6.1) gives a good representation of a softwood lignin, while Figure 6.2 proposes a structure for sulphomethyl kraft lignin.

Lignin in its natural form is insoluble in neutral liquids and organic solvents. The two most commonly used methods of separating cellulose and lignin are described briefly below.

(a) *Sulphite pulping.* One way of separating cellulose from lignin and other compounds is to treat wood chips with a hot acid solution of calcium bisulphite. During this digestion process part of the lignin becomes sulphonated, while simultaneously some linkages become hydrolysed. Hydrolysis causes the lignosulphonate molecules to dissolve, together with other soluble compounds such as sugars.

(b) *Kraft pulping.* Another method of separating lignin from cellulose is to treat the wood chips with a hot alkaline solution of sodium salts; the pH

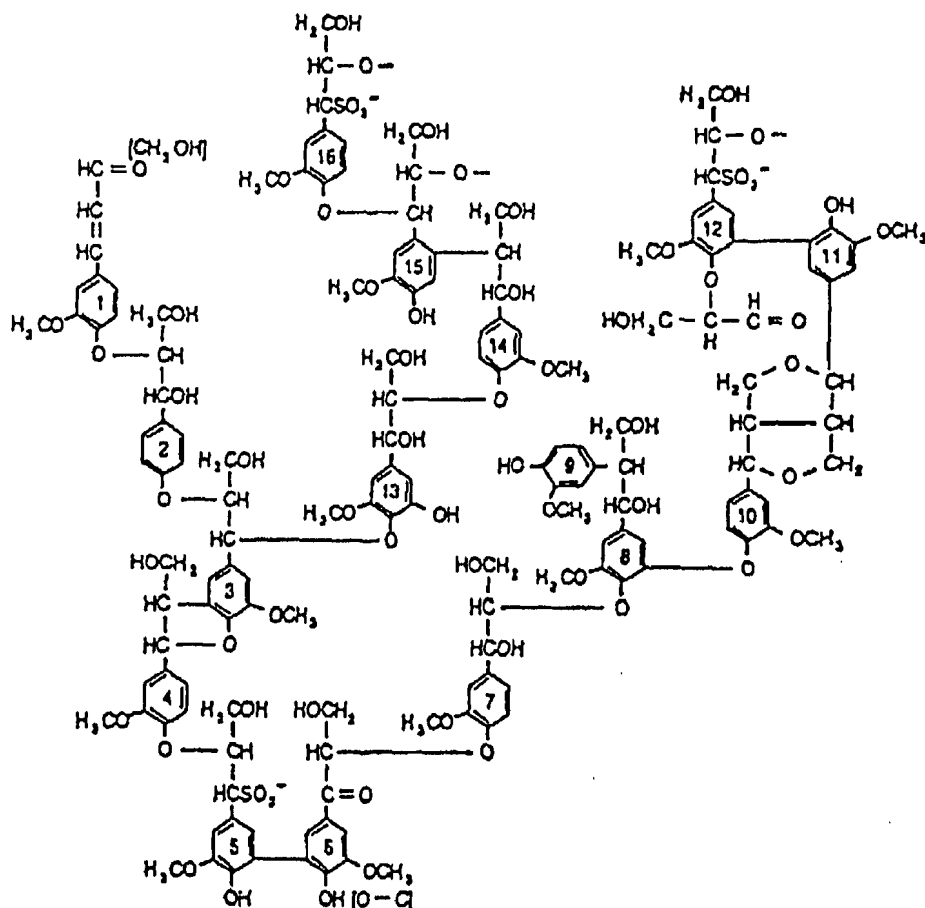


Figure 6.1 Structural model of softwood lignosulphonate.

of this solution is around 13–14. The resultant liquor contains lignin that is totally dissolved, and hemicellulose that is only partly dissolved.

6.1.2 Lignin modification

The lignosulphonate molecule can be modified by a variety of chemical processes. It is possible to enhance selectively certain properties and tailor-make lignosulphonates for specific applications. This has allowed the commercial development of a range of speciality high-performance chemicals that show similar broad characteristics while being distinctly different in their specific properties.

Figure 6.3 illustrates the different molecular weight distribution characteristics as a function of chemical modification. Compared to the standard refined product BORRESPERSE NA, it highlights the shift towards a higher mean molecular weight with the ultrafiltrated product UFOXANE 3A, and the much tighter distribution characteristic of an oxylignin such as VANISPERSE CB.

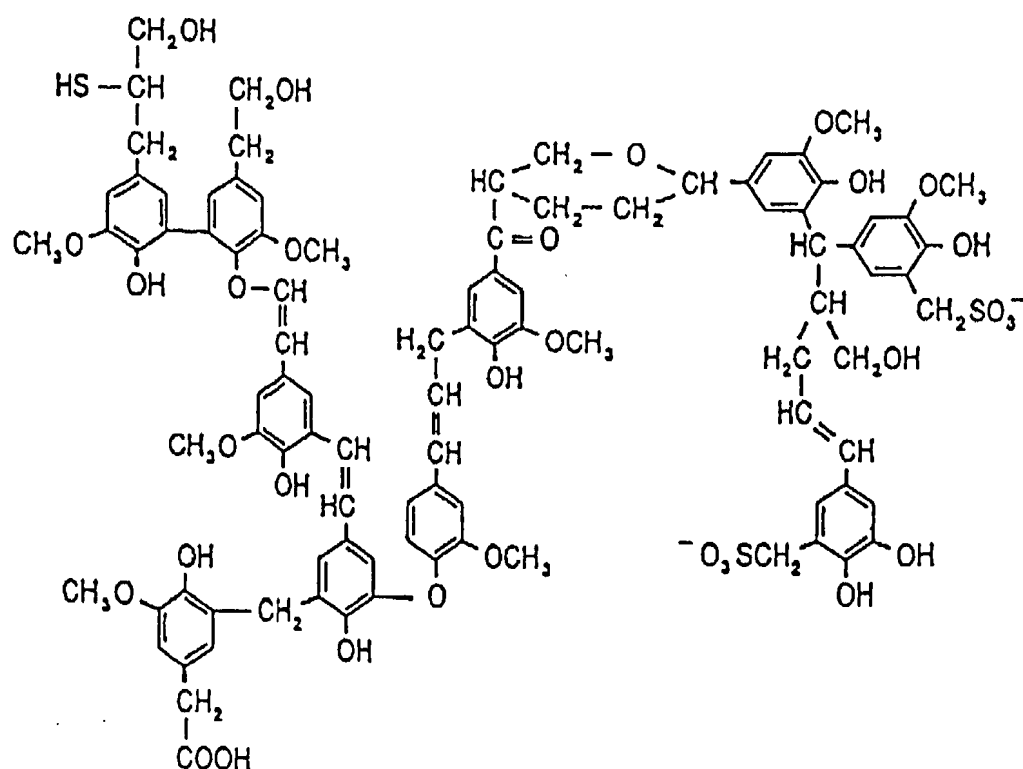


Figure 6.2 Structural model of sulphomethyl kraft lignin.

6.2 Wettable powders (WP)

The methodology and technology involved in developing a WP is mature, and well understood. The dust problems associated with wettable powders have resulted in them being superseded by suspension concentrates (SC) and water-dispersible granules (WG). However, WPs still offer a viable formulation system, and the recent advent of water-soluble packaging has given a new lease of life to many WP formulations.

6.2.1 Formulation

(a) *Active ingredients.* Individual active ingredients will have different milling requirements, but as a general rule the best results are obtained when all the components (if their physical form allows) are preblended with the active ingredient before milling. It is important to keep the particle size distribution as narrow as possible, otherwise powder compacting can lead to poor wetting and dispersing characteristics. Liquid active ingredients must be absorbed on a suitable carrier prior to the preblending stage.

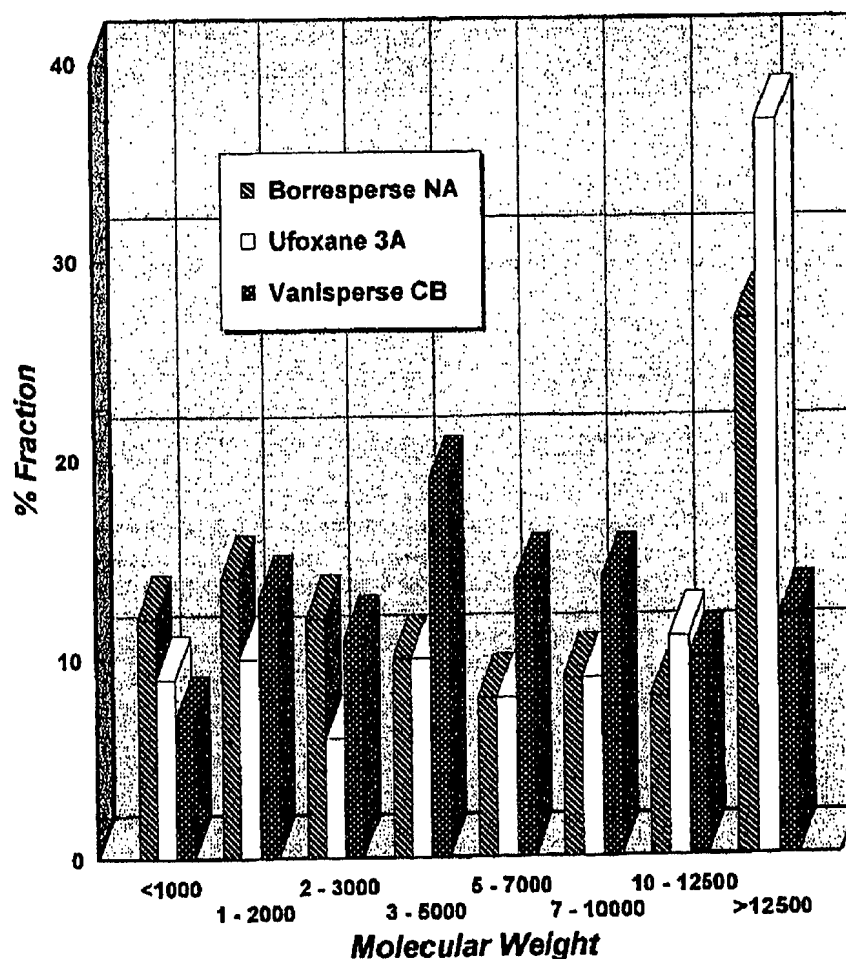


Figure 6.3 Molecular weight characteristics as a function of chemical modification, for three product types.

(b) *Fillers.* A wide range of fillers is available to the formulator, both natural and synthetic. The particular physical and chemical properties of a WP system will dictate the selection, and it is not necessary to go into such detail here. Suffice to say that all the fillers currently used are compatible with lignosulphonate dispersants.

(c) *Anti-caking agents.* If the active ingredient has a low melting point, or the loading of the active ingredient is high, an anti-caking agent will assist the grinding process and improve the flow characteristics of the WP, both of which improve the final suspensibility. Many of the carriers used to absorb liquid active ingredients also function as anti-caking agents.

(d) *Wetting agents.* The combination of lignosulphonate dispersants and sodium alkylnaphthalene sulphonate works well for most active

ingredients, but occasionally a non-ionic ethoxylate may be more effective. The synergy observed between lignosulphonate dispersants and a wetting agent can permit the use of reduced amounts of these higher-cost components.

(e) *Dispersants.* Lignosulphonate dispersants have a long association with the formulation of WPs, and these products are used for formulating a wide range of pesticide active ingredients. High dispersion efficiency coupled with economy of use make them an obvious choice. The extensive range of commercially available lignosulphonates includes products with differing degrees of sulphonation and molecular weight distribution. The significance of these two characteristics lies in the differing hydrophobic nature of pesticide active ingredients. A certain amount of trial and error will always be necessary, but generally the more hydrophobic active ingredients require a dispersant with a lower degree of sulphonation, and higher mean molecular weight.

This effect is well illustrated in Figure 6.4, which shows increased suspensibility of an 80% sulphur WP as a function of dispersant type and concentration. As an example, the series Borresperse NA, Ultrazine NA and Ufoxane 3A is in order of increasing dispersant hydrophobicity (which is derived from their respective methods of manufacture). The ultrafiltrated (high molecular weight) and desulphonated Ufoxane 3A has a greater affinity for the hydrophobic sulphur. This allows a higher level of interaction and subsequent dispersion efficiency.

(f) *Water-soluble packs.* Experimental work has shown that lignosulphonate's dispersion performance is not affected by the presence of the dissolved polymers used in water-soluble films, nor do they affect the disintegration rate of these films in water.

6.2.2 Production methods

(a) *Solid active ingredients.* Where physical form allows, all powder components should be preblended prior to milling, though it may be necessary to pregrind the active ingredient. The blended material is then milled in a pin mill or air-jet mill. Experience has shown that lignosulphonate dispersants assist the milling process by becoming adsorbed onto the crystalline active ingredient, thus increasing electrostatic repulsion and improving milling efficiency. This can also be of assistance when milling lower melting point active ingredients.

(b) *Liquid active ingredients.* Liquid technical (active) ingredients and liquid or waxy wetting agents must be incorporated into a carrier, by spraying onto the absorbent in a suitably equipped blender. The wetting and

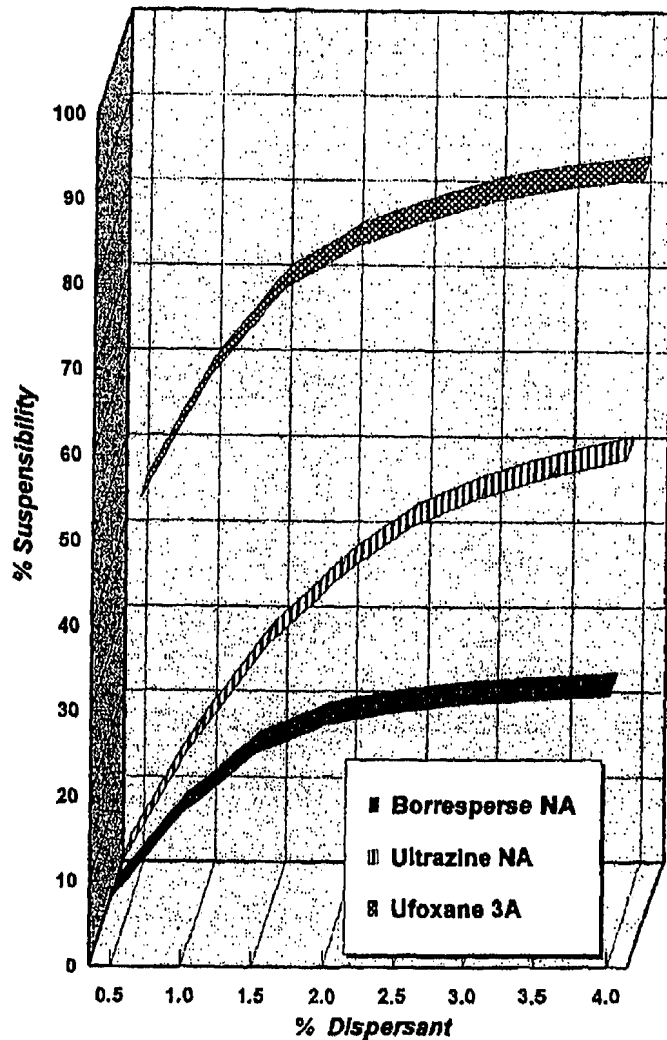


Figure 6.4 Suspension of 80% sulphur wettable powder as a function of dispersant type and concentration.

suspension of the WP may be improved by incorporating the wetting agent into the absorbent before the liquid technical ingredient. The remaining powder ingredients including the lignosulphonate are then added, and the blend then milled by standard techniques.

Table 6.1 presents some typical examples of WP formulations.

6.3 Water-dispersible granules (WG)

This type of formulation is becoming increasingly popular, due mainly to the requirement to improve the safety and efficiency of dosing and handling. A WG can be regarded as the granular form of a wettable powder,

Table 6.1 Typical WP formulation examples (wt%)

Active ingredient		Lignosulphonate dispersant ^a				Wetting agent ^b		Fillers etc.	
		A	B	C	D	A	B	Anticaker	Kaolin
Captan	85	2				3			to 100
Carbendazim	50		4			1			to 100
Diuron	80		4				2		to 100
Malathion	50				6		3	30	to 100
Mancozeb	80	3				1			to 100
Sulphur	80			3		1		4	to 100

^a Dispersants: A = Borresperse NA; B = Ufoxane 3A; C = Vanisperse CB; D = Polyfon H.
^b Wetting agents: A = Naphthalene sulphonate; B = Non-ionic ethoxylate.

and lignosulphonate dispersants are an invaluable aid to the formulator looking to develop WG from existing WP formulations or new novel WG applications.

6.3.1 Formulation

(a) *Active ingredients.* When using solid active ingredients it is necessary to mill the technical component to obtain a particle size of 1–10 µm. However, it is important to optimize the particle size distribution. If the distribution is too broad, the particles become closely packed and redispersibility of the granule is impaired. Also, if the active ingredient is milled too finely, a disproportionate amount of dispersant will be required to obtain good suspensibility. Liquid active ingredients can also be formulated if they are first adsorbed onto a silica carrier, though selection of the optimum granulation method then becomes more important.

Lignosulphonate products have also been found to function as grinding aids. The dispersant becomes adsorbed onto the crystalline active ingredient, and by increasing the electrostatic repulsion between the crystals it helps the grinding media function more efficiently. In addition, if the dispersant is present in the grinding stage, the final suspensibility of the WG will usually be improved.

(b) *Wetting agents.* The sodium alkylnaphthalene sulphonates are found to work well in combination with lignosulphonate dispersants for most formulations. However, in certain cases an ethoxylated block copolymer type may be the choice.

(c) *Fillers, carriers and disintegrators.* Individual formulation recipes and their mode of manufacture can have a distinct effect on the final properties

of a WG, and precipitated silicas have been found to be effective (as grinding aids or carriers). The balance of filler, whether it is kaolin or a disintegrating agent, is left to the formulator's discretion, though experience has shown that these materials function well in combination with lignosulphonate dispersants. In addition, it is worth mentioning that although lignosulphonates are not true disintegrating agents, selection of the correct lignosulphonate dispersant will greatly assist redispersibility and granule spontaneity.

The best formulations are usually those that contain the lignosulphonate dispersant that gives the best balance between redispersibility and dispersion efficiency.

(d) *Binders*. Lignosulphonates are very effective hydrophilic binders, forming an inactive film binding system. They are particularly useful in developing WG formulations as they combine both binding and dispersing properties.

(e) *Dispersants*. The wide range of lignosulphonate dispersants commercially available is suitable for formulating a wide range of pesticide actives as WGs. The formulator can find products with varying degrees of sulphonation and varying molecular weight distribution. The significance of these two characteristics lies in the differing hydrophobic nature of pesticide actives. A certain amount of trial and error will always be necessary, but as a general rule the more hydrophobic active ingredients require a dispersant with a lower degree of sulphonation, and a higher mean molecular weight.

Occasionally a lignosulphonate dispersant will function best when used as a codispersant. Among some of the effective combinations known are their use with polycarboxylates and naphthalene sulphonate derivatives.

In addition to traditional trial-and-error techniques, quantification of the relative affinity of a dispersant for the pesticide substrate being dispersed can give invaluable information [1, 2]. This can also aid future formulation studies, by characterizing more precisely the performance of a surfactant system. Figure 6.5 shows adsorption isotherms obtained by the serum replacement method for a herbicide-lignosulphonate system. It clearly shows the higher level of surface adsorption for a sulphomethylated kraft lignin with a low degree of sulphonation (e.g. Reax 85A from Westvaco or Diwatex 40 from Borregaard), compared to a standard refined product such as Borresperse NA. Although these isotherms were obtained for dilute systems containing only the dispersant and active ingredient, the higher level of adsorption can be extrapolated to increased dispersion efficiency in a finished formulation.

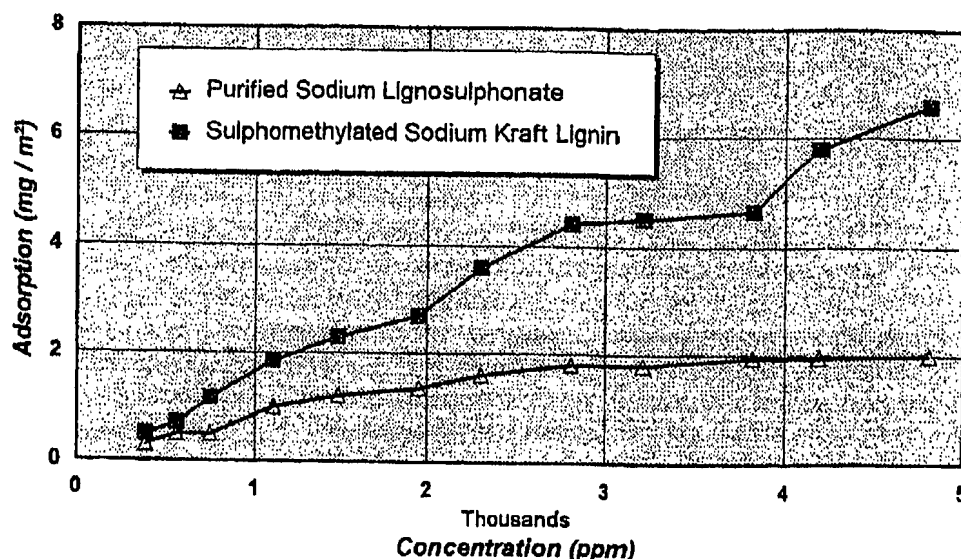


Figure 6.5 Surface adsorption on Diuron as a function of product type and concentration.

6.3.2 Production methods

Lignosulphonate dispersants are used to formulate WGs by all the common granulation processes, and no particular limitations are encountered when selecting a product for use in a certain process. However, one formulation recipe will give different granule characteristics depending on the granulation method employed, and minor modifications to the initial recipe can improve the final properties of the WG.

(a) *Pan granulation.* Although pan granulation gives a product with good redispersion properties, they often have poor resistance to handling. If however, during the final stages of granulation a small quantity of lignosulphonate is sprayed onto the pan, the granule surface will become more tightly bound and have less tendency to dust. A slight increase in redispersion time may occur but this will not be enough to detract from the WG's essential properties.

(b) *Fluid bed granulation.* WGs made by this process share much the same properties and corresponding drawbacks as those made by pan granulation. The final product has excellent disintegration properties, but this also means that it is the least resistant to handling, and it is often necessary to use a lignosulphonate in the granulating fluid to aid agglomeration and final hardness.

(c) *Spray drying.* Generally spray drying produces easily redispersible granules. However, to minimize the effects of surfactant migration

(which can give poor handling resistance and inferior redispersibility), the insoluble solids content of the atomizer feedstock should be as high as possible.

Use of a high-performance lignosulphonate dispersant will keep the feedstock sufficiently fluid, even with a high solid loading.

The wide range of lignosulphonate dispersants commercially available are particularly effective as dispersants for spray-dried formulations, and the product Ufoxane 3A from Borregaard is worthy of special attention. Experience has shown lignosulphonate dispersants of this type to have excellent heat stability, and spray-dried WG formulations containing them show higher suspensibilities than those made with other lignin types or some synthetic dispersants.

(d) *Extrusion granulation.* Obtaining good WG properties by extrusion requires a rather different approach compared to the other methods. Granule durability is not a problem, and indeed must be limited if the WG is to have acceptable redispersibility. It is important to optimize the level of dispersant required to suspend the active ingredient, so that the total binder content of the system is kept to a minimum. Normally lignosulphonate products have a sufficiently high rate of dissolution, but if greater redispersibility is required a suggested combination is a lignosulphonate dispersant (high dispersing/low binding grade) with an auxiliary binder of very high dissolution, or addition of a suitable disintegrating agent. In all cases the moisture content of the extruder feedstock is vital. Too high a moisture content will result in granules with an almost closed or impervious surface. If a relatively dry mix is used, the extruded granules have a rougher texture, and a much higher surface area available for wetting.

Table 6.2 gives examples of WG formulations.

6.4 Suspension concentrates (SC)

The absence of dust and solvents, combined with the ease of handling that SCs offer, has made them justly popular. However, recent initiatives on the disposal of used packaging may limit significant further development of SC formulations in some agrochemical markets.

6.4.1 Formulation

(a) *Active ingredients.* One of the drawbacks of the SC system is that it is not suitable for every type of active ingredient. The main criterion for a suitable active ingredient is that it must be practically insoluble in the water phase. Problems of crystal growth (Ostwald ripening) during storage can

Table 6.2 WG formulation examples (wt%)

Active ingredient	Lignosulphonate dispersant ^a				Wetting agents Co-dispersants ^b			Fillers etc.		Production method ^c
	A	B	C	D	A	B	C	Anticaker	Kaolin	
<i>Bacillus thuringiensis</i>	80			8	3				to 100	PG
Carbendazim	80		6		2		5		to 100	FB
Copper hydroxide	80			20						SD
Chlortoluron	80	12					8			FB
Diuron	80		12			3			to 100	EX
Mancozeb	75	15			3				to 100	SD
Simazine	90		8		2					EX
Thiram	85		9		3			3	to 100	PG

^a Dispersants: A = Borresperse NA; B = Reax 85A; C = Ufoxane 3A; D = Ultrazine NA.
^b Wetting agents: A = Naphthalene sulphonate; B = Non-ionic ethoxylate; C = Polycarboxylate dispersant.
^c Production Method: PG = pan granulation; FB = fluid bed granulation SD = spray drying; EX = radial extrusion.

occur even at very low levels of solubility. The latter problem can be minimized if the dispersants employed are also good crystal growth inhibitors, and there are a number of commercial lignosulphonate dispersants that function very effectively in this area.

(b) *Wetting agents.* It will not always prove necessary to use a wetting agent in combination with lignosulphonate dispersants. However, if milling problems are encountered, the addition of a small quantity of an ethoxylated block copolymer wetting agent will often smooth the process.

(c) *Dispersants.* In an SC system, stability against irreversible flocculation can be achieved by use of high-performance dispersants. A polyelectrolyte material such as lignosulphonate prevents flocculation in two ways:

- electrostatic repulsive forces are generated by the presence of an electrical double layer at the particle-solution interface [3];
- steric repulsion, arising from the apparent expansion of the particle due to the adsorbed dispersant [4].

The latter effect is more prevalent with dispersants of higher mean molecular weight and a lower degree of sulphonation. However, other factors can also have influence and experience has shown that more detailed experimental work into the nature and degree of the pesticide-dispersant interaction (as mentioned in the WG section) can greatly assist selection of the optimum surfactant system [5]. Figure 6.6 illustrates the significant

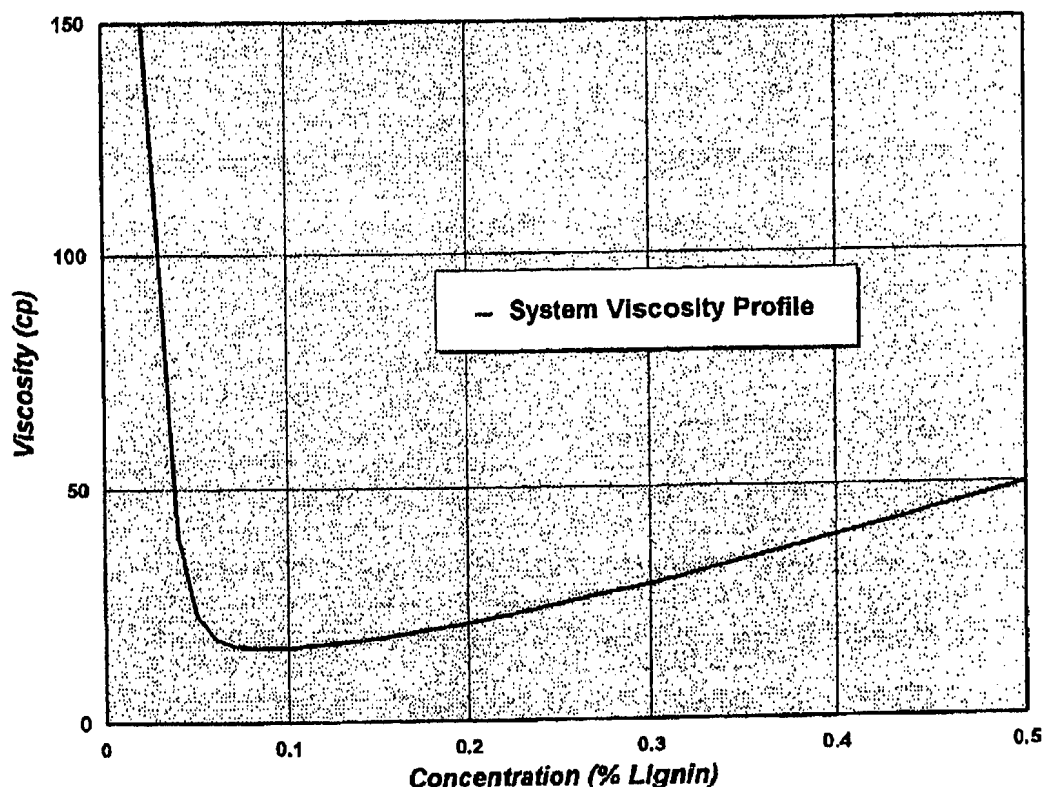


Figure 6.6 Effect of dispersant concentration on the viscosity of a 59% kaolin clay slurry.

decrease in slurry viscosity for a typical high-solids suspension when using a lignosulphonate dispersant.

(d) *Thickeners.* The purpose of thickening agents is to achieve sufficient long-term stability by means of gravitational stabilization; this prevents sedimentation and keeps the active in suspension. SC formulations are often stabilized by anti-settling agents such as xanthan gum and bentonite or smectite clays, either alone or in combination. Individual experiments are required to balance the effect of dispersant viscosity reduction, and the thickening of the system by gravitational stabilization.

Solutions containing xanthan gum can be prone to bacterial degradation, and it is important that a suitable biocide is incorporated.

(e) *Anti-freezing agents.* Monoethylene glycol (MEG) and monopropylene glycol (MPG) are suitable for use with lignosulphonates, but caution must be exercised to ensure the active ingredient is not soluble in the antifreeze as this can lead to crystal growth problems.

(f) *Anti-foaming agents.* The physical and chemical nature of the SC system will dictate the selection of the best anti-foaming agent. Polysiloxanes

have been found to work well in combination with lignosulphonate dispersants.

6.4.2 Production methods

The surfactant system of a SC performs four major tasks during production.

(a) *Particle wetting.* Low molecular weight surfactants and lignosulphonates help to bring about the rapid conversion of the coarse technical component into a form that can be efficiently milled by prewetting the active.

(b) *Efficient milling.* After the initial wetting of the active ingredient, the surfactant then becomes adsorbed onto the particle surface. As the mechanical breakdown of the active ingredient proceeds, the available surface area also increases, and in order to maintain a sufficiently low viscosity the lignosulphonate becomes adsorbed onto the newly created particle surfaces, and stops reagglomeration of the active ingredient. At this point care must be taken, since over-grinding or an insufficient level of dispersant will give a total surface area in excess of the capacity of the dispersant, and the viscosity can increase very quickly.

(c) *Prevention of flocculation.* The adsorbed lignosulphonate generates forces of repulsion to counter the van der Waals attractive forces of the dispersed active, which will otherwise lead to agglomeration and flocculation. Long-term stability is achieved by the use of additional gravitational stabilizers.

(d) *Maintaining a manageable viscosity.* At certain stages of production, and especially at the final product packaging the SC must be in a form where it flows easily and can be pumped without difficulty (Figure 6.6).

(e) *Rheological properties.* The rheological behaviour of SC systems is worthy of closer study, as a way of fine tuning a formulation to give the optimum balance between suspension stability and product viscosity. The example selected here is a 450 g/l Carbendazim SC that utilizes a combination of both organic (xanthan gum) and inorganic (smectite clay) thickening agents. These two materials actually display quite different rheological properties, the combined effects of which can give beneficial properties to an SC formulation.

An SC formulation must have a sufficiently high viscosity to protect it against sedimentation during storage, but the viscosity must not be so high that the product is difficult to handle or shows insufficient 'bloom'. Figure 6.7 shows viscosity as a function of shear stress for the Carbendazim SC system using two different lignosulphonate dispersants.

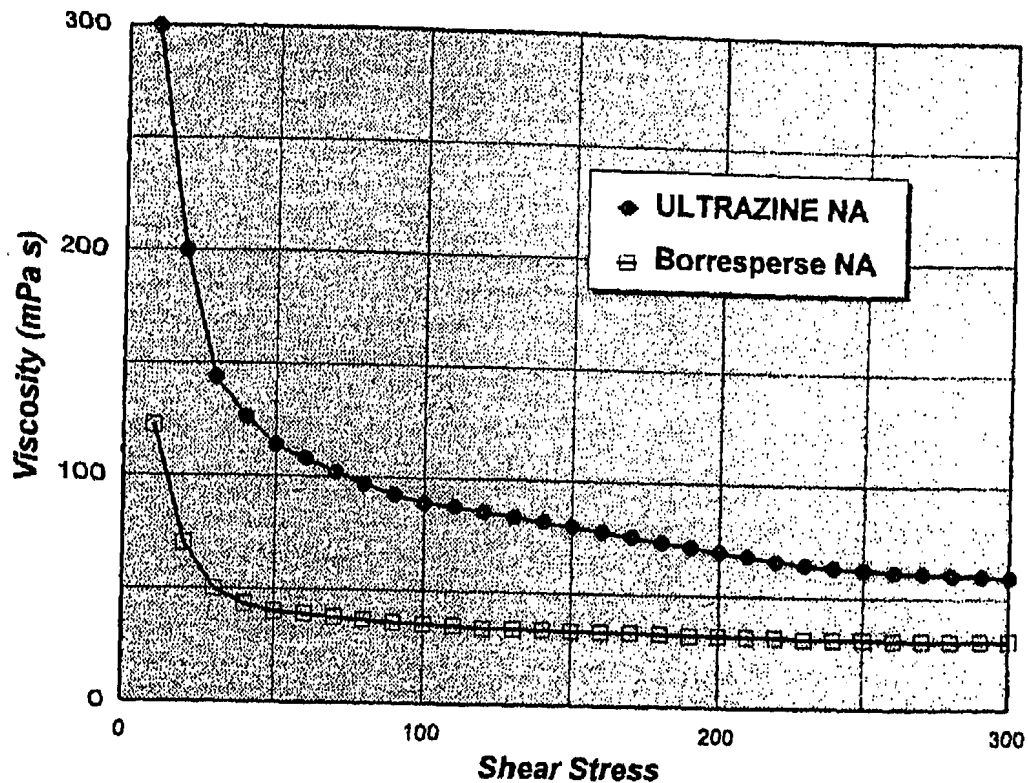


Figure 6.7 Effect of shear stress on viscosity for Carbendazim 450 SC.

The system using Ultrazine NA shows sufficient thixotropic behaviour for the suspension stability to be maintained during storage. However, since the system also displays pseudoplastic behaviour, the viscosity drops dramatically when slight shear is applied. As a result of this the formulation containing Ultrazine NA is easier to both handle and store.

Table 6.3 presents formulations for SCs using speciality lignosulphonate dispersants.

Table 6.3 SCs formulated with speciality lignosulphonate dispersants (g/l)

Active ingredient	Lignosulphonate dispersant ^a				Wetting agent ^b		Thickeners ^c			Other additives		
	A	B	C	D	A	B	A	B	C	MPG	Antifoam	Water
Atrazine	500	40			2.0	1.0				50	2.0	to 1L
Carbendazim	450			30	0.5	0.5			3.0	50	2.0	to 1L
Chlortoluron	500			30	1.0	0.5			4.0	50	2.0	to 1L
Sulphur	800	40			4.0	2.0				50	2.0	to 1L
Ziram	500		25			2.0	4.0			50	2.0	to 1L

^a Dispersants: A = Borresperse NA; B = Renx 85A; C = Ufoxune 3A; D = Ultrazine NA.

^b Wetting agent: A = Non-ionic ethoxylate.

^c Thickeners: A = Xanthan gum; B = Bentonite; C = Veegum.

6.5 Oil-in-water emulsions (EW)

6.5.1 Formulation

The main difference between EWs and ECs is that in the former some or all of the solvent is replaced with water, and it is the growing desire to reduce solvent use in agricultural applications that has resulted in increasing interest in EW formulations in recent years. This type of formulation is particularly useful for liquid active ingredients that are not easy to absorb onto a carrier, and low melting point solid active ingredients that cannot be finely milled to produce a suspension concentrate.

The stabilization of emulsions by lignosulphonates is a result of adsorption at the oil-water interface, establishing electrostatic repulsive forces and a semi-rigid film.

The presence of this semi-rigid film contributes significant mechanical stability to these emulsions. Lignosulphonate dispersants are very effective in stabilizing immiscible liquids in water to give oil-in-water emulsions. These emulsions are resistant to variations in pH, temperature variations, high electrolyte concentrations and ageing. It is not recommended to use lignosulphonates in combination with other surfactants and emulsifiers when producing EWs, as compatibility problems can arise due to competing stabilization mechanisms.

6.5.2 Production methods

Lignosulphonate dispersants stabilize EW formulations by preventing the coalescence of the suspended oil-solvent phase containing the active ingredient. Lignosulphonates do not significantly lower the surface and interfacial tensions, so the oil phase must be first subdivided in a homogenizer to obtain a fine-grained emulsion which is then added to the dispersant solution under further homogenization to produce the oil-in-water emulsion.

6.6 Controlled release

The mode of action of a controlled-release formulation is often tailored very specifically to a particular application, and as such use a wealth of different techniques and technologies.

The diversity and selectivity of controlled release systems means that they deliver a wide range of quite specific features to their individual applications. However, it can be said that they all aim to fill the following criteria:

- improve efficiency;
- use no toxic solvents and inert components;

- reduce phytotoxicity;
- reduce environmental impact;
- limit groundwater contamination;
- reduce health risks during production and use.

Lignosulphonates and their many modified forms offer great versatility for developing tailor-made controlled-release mechanisms. As an example, lignin can be adapted to give varying degrees of solubility, polarity, compleximetry and porosity, etc.

6.6.1 Granules

The traditional granule formulation is a crude form of controlled release in that it can have a longer effective pest control period than spray application. Lignosulphonates are effective binding and agglomeration aids in granule production, forming an inactive film binding system. They also combine dispersion ability with good resistance to caking of the agglomerated product. The controlled-release capabilities of a granule can be refined by addition of agents to either speed up or slow down the rate of diffusion into the soil. Varying the quantity of binder can impart different rates of granule disintegration.

6.6.2 Tablets

Lignosulphonates offer two important characteristics to the chemist developing controlled-release tablets:

- as a naturally occurring polymer lignin is environmentally benign, and is classed as inherently biodegradable, offering possibilities for use as a controlled-release matrix;
- high dispersion power; high-performance lignosulphonate dispersants can be used to modify the release rate of the active ingredient from the tablet.

6.6.3 Gels

The ability to produce crosslinked gel structures by modifying lignin with a suitable crosslinking agent offers many possibilities. These gels display a high degree of reswellability in water, of particular use when formulating water soluble pesticides such as 2,4-D, though water-insoluble active ingredients can also be formulated by pretreatment with a suitable solvent. The release rate can be tailored to a specific application, from a dump release mechanism right through to an extended period of continuous uniform release.

The inclusion of absorbent fillers for volatile active ingredients or void-

creating materials into the gel matrix can have a pronounced effect on the absorptive characteristics of the gel, allowing a greater range of pesticide actives to be formulated in this manner.

Which crosslinking agent used is also important in terms of the absorptive capacity of the gel. Typically a formaldehyde crosslinked gel will swell to around six times its dry weight, whereas epichlorohydrin gels show roughly half this capacity. Selection of the crosslinking agent will also be dictated by the desired release rate.

6.6.4 Microencapsulation

At present this is the most important of the controlled release methods, and has seen the greatest commercialization. The principal methods for producing microcaps with lignosulphonates are by processes of coprecipitation. There are numerous documented methods for producing microcaps in this way, but a general method is as follows:

1. prepare a lignosulphonate/emulsifier solution;
2. incorporate the active into the aqueous phase;
3. mix to form an emulsified dispersant-active ingredient system;
4. precipitate the solution with a mineral acid or polyvalent salt;
5. harden the microcaps by pH buffering;
6. separate and concentrate;
7. process into desired formulation type.

Selection of the most suitable lignosulphonate will depend on many factors, including the physical and chemical nature of the active ingredient, the target pest and the controlled-release period required. This can be illustrated by two examples.

- Microencapsulation of a stomach contact insecticide (e.g. Carbosulfan). The lignin-encapsulating polymer will be insoluble at neutral or acidic pH, as found in normal soil contact. However, the lignin will be soluble in the alkaline pH environment of an insect's digestive system, thereby providing very specific release conditions.
- The soil mobility of the herbicide Atrazine can be controlled when encapsulated with a lignosulphonate of low solubility and high molecular weight. Certain lignosulphonates have a high adsorptive capacity for Atrazine, providing a ready mechanism of controlled release, and also help to limit leaching into groundwater.

As well as providing the encapsulating polymer, the presence of a lignosulphonate dispersant can greatly improve the microcap's efficiency and fine tune the ultimate release rate. Systems have been investigated where one material provides both the encapsulation media and the dispersant.

The diverse and selective nature of controlled-release mechanisms, particularly in the area of microencapsulation, means it is difficult to give an exhaustive list of all the modified forms of lignin available to the pesticide formulator. However, it should be stated that the versatility of lignin for such specialized delivery systems has probably not yet been fully exploited.

6.7 Ultraviolet protection

Many biopesticides, pesticide active ingredients and agrochemical agents are susceptible to decomposition when exposed to UV radiation from sunlight. The active ingredient can be rendered biologically inactive by UV-initiated or catalysed degradation.

An important part of lignosulphonates' versatility as controlled-release matrices is that, due to their high aromatic content, lignin derivatives show excellent UV absorption properties. The range and degree of UV absorbance changes as a function of the chemical bonds and groups present in the lignin molecule (Figure 6.8).

One procedure is to encapsulate the pesticide active ingredient in a wall material consisting of lignin or a lignin-gelatin complex. Water-soluble active ingredients can also be protected in this manner by the emulsification in water of an active ingredient, lignin and gelatine mixture prior to encapsulation. As an example, the photolytic degradation of the pyrethroid

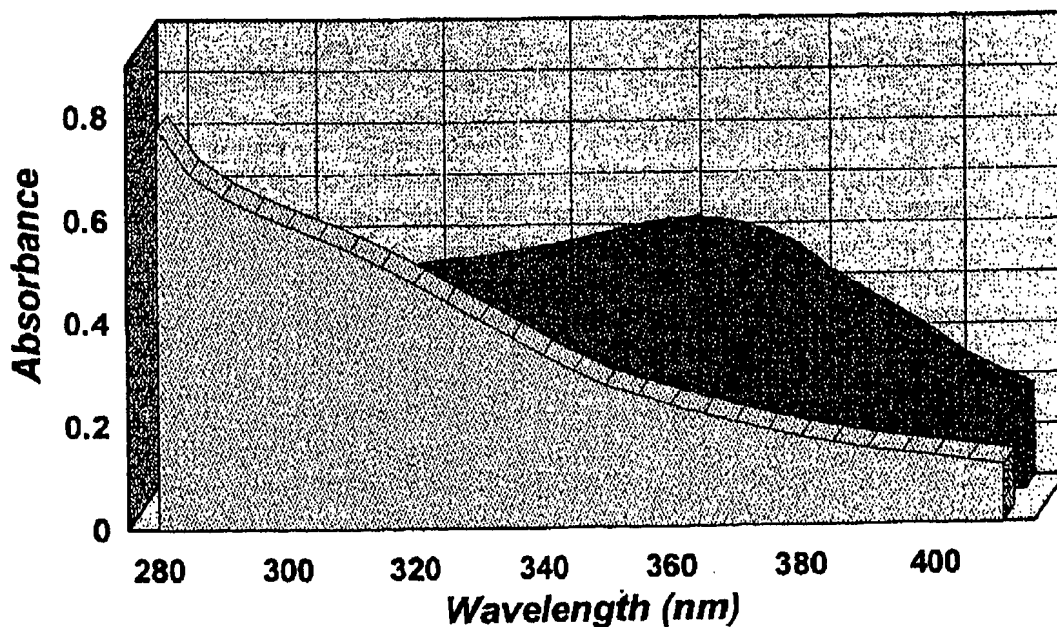


Figure 6.8 Ultraviolet absorbance by lignin as a function of wavelength.

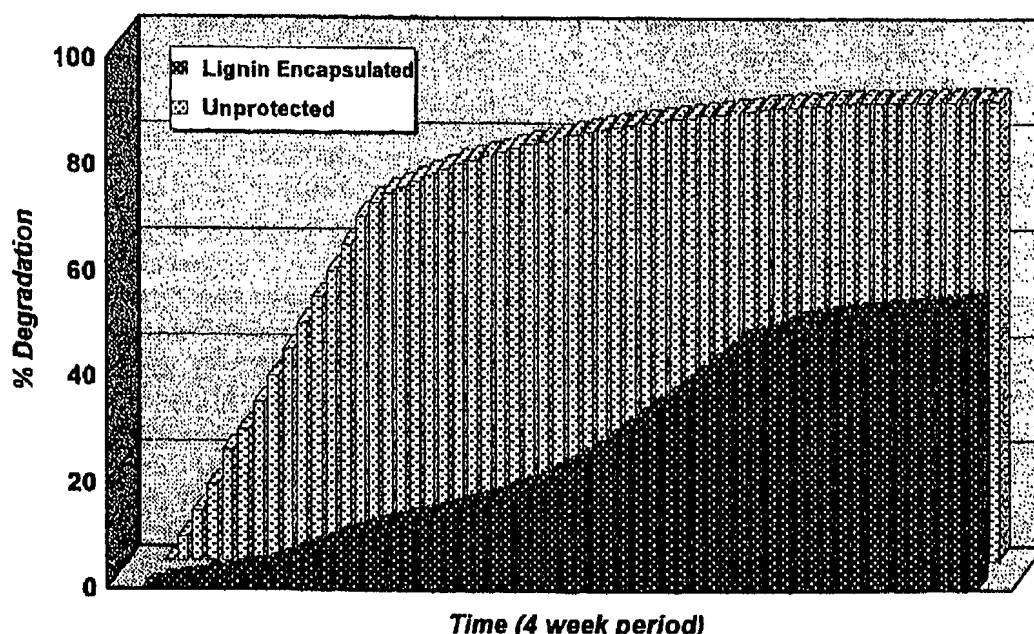


Figure 6.9 Ultraviolet protection of Parathion: degradation versus time.

insecticide Permethrin, can be reduced by up to 50% over a 2-week period. Figure 6.9 gives another example, showing the increase in UV protection of Parathion when encapsulated with a specifically modified lignosulphonate.

6.8 Compatibility agents

In order to reduce expensive multiple applications, it is often desirable to combine the application of liquid fertilizer and pesticide. The stability and compatibility of the resulting tank mix must be ensured. The use of high-performance lignosulphonate dispersants gives good compatibility, and allows efficient uniform application.

6.9 Adjuvants

The true potential for lignosulphonates and their derivatives as adjuvants has probably not yet been fully recognized. Lignosulphonates show many of the basic properties required of an adjuvant, and their presence as formulation additives can assist efficacy. However, there could be further possibilities, for example the use of high molecular weight derivatives as spray control additives.

The use of lignin derivatives as tank-mix additives is a potential develop-

ment area, and interest should increase as the inventory of chemicals used in agriculture comes under even greater scrutiny.

6.10 Complexing agents

Where problems of hard water occur, it is advantageous if the lignosulphonate dispersant employed also exhibits chelating and sequestering properties. Lignosulphonates can be regarded as complexing agents, though chemical nature and specific modification mean that certain products are more effective. Products such as Reax 100M from Westvaco, and Marasperse AG from Borregaard, have been specifically developed to have superior complexing abilities.

6.11 Environmental and regulatory information

Environmental issues for lignosulphonate products can be divided into two areas:

- health and safety of personnel handling the products;
- effect of the products on the natural environment.

6.11.1 Personnel

Toxicological studies carried out on lignosulphonate products (including chemically modified variants), together with over 50 years of experience in use, have shown them generally to be non-toxic and non-irritant. No human health problems are attributable to long-term exposure to lignosulphonates.

6.11.2 Environmental

Lignosulphonates have been applied to roads, used in animal feeds, and a host of other applications where the final product comes into contact with human foodstuffs, for more than 30 years without deleterious effects.

Standard lignin products have the following properties:

- no dioxins present; no other organics are present at dangerous levels;
- toxic trace minerals are below EPA toxicity limits (as set by the US Environmental Protection Agency);
- a low order of toxicity towards fish;
- non-toxic orally, and non-irritating to the skin and eyes of animals;
- very low toxicity towards plant life: studies have shown that lignins are not phytotoxic to plant foliage and root systems;
- residuals are resistant to decay;

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- they are a renewable and strictly managed resource.

Even when spread on land there is little risk of groundwater contamination. Published data indicate that at less than 10 kg/m², no environmental damage occurs.

Lignosulphonates do not solubilize toxic heavy metals and transport them to the groundwater. Lignosulphonates form insoluble salts with heavy metals.

The US Food and Drug Administration has issued regulations for the safe use of lignosulphonates in agrochemical formulations:

1. as adjuvants in pesticide chemical formulations exempt from requirements of tolerance when applied pre- or post-harvest: 21 CFR 182.99, 40 CFR 180.1001, section (c);
2. exempt from requirements of tolerance when used as ingredients in pesticide formulations applied to animals: 40 CFR 180.1001, section (e);
3. as dispersants or stabilizers in pesticides applied pre- or post-harvest to bananas: 21 CFR 172.715.

The relevant EPA registration numbers are as follows:

Calcium lignosulphonates	B-058-1511
Sodium lignosulphonates	B-058-1486
Ammonium lignosulphonates	B-058-1956

The *Chemical Abstracts* series numbers are:

Calcium lignosulphonates	CAS 8061-52-7
Sodium lignosulphonates	CAS 8061-51-6
Ammonium lignosulphonates	CAS 8061-53-8

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H. T. Delli Colli¹ and Ingomar W. Doering²

The Physical Chemistry of WDGs: Porosity and Surfactant Dissolution as a Function of Dispersant Molecular Weight

Reference: Delli Colli, H. T. and Doering, I. W., "The Physical Chemistry of WDGs: Porosity and Surfactant Dissolution as a Function of Dispersant Molecular Weight," *Pesticide Formulations and Application Systems: Twentieth Volume, ASTM STP 1400*, A. K. Viets, R. S. Tann, and J. C. Mueninghoff, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: The speed and completeness of the disintegration of water-dispersible granules depend upon several factors. Two of the most important are the porosity of the individual granules and the rate of dissolution of the surfactant package within the formulation.

The present work represents a small piece of a larger overall effort designed to explore the physicochemical aspects of WDG development. An objective of the larger effort is the enablement of the formulation chemist to identify key compositional and production related parameters for WDGs early enough in the development process to significantly shorten it.

Keywords: Paste Rheology
Extrusion
WDG

Introduction

The successful development of an agrochemical formulation is a journey into the world of practical applied colloid and surface chemistry. This having been stated, the physicochemical properties of the formulation and its components are the signposts for the trip.

When applying this concept to dispersants, and in particular polyelectrolytes such as lignosulfonates, one cannot help but be drawn to the conclusion that molecular weight is one of the more important of these properties. Molecular weight plays a role in determining the level of interfacial activity of a dispersant, it helps regulate the rate at which a material dissolves, and it plays both direct and indirect roles in determining and controlling the rheology of the system or formulation in which a particular dispersant is

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placed. These basic physicochemical processes in turn strongly influence many of the properties of formulations and the processes by which they are manufactured, as well. This is demonstrated in Figure 1. Here, the performance variables of an extruded water dispersible granule are listed along with the known relationships between dispersant molecular weight and the processes which bring them about.

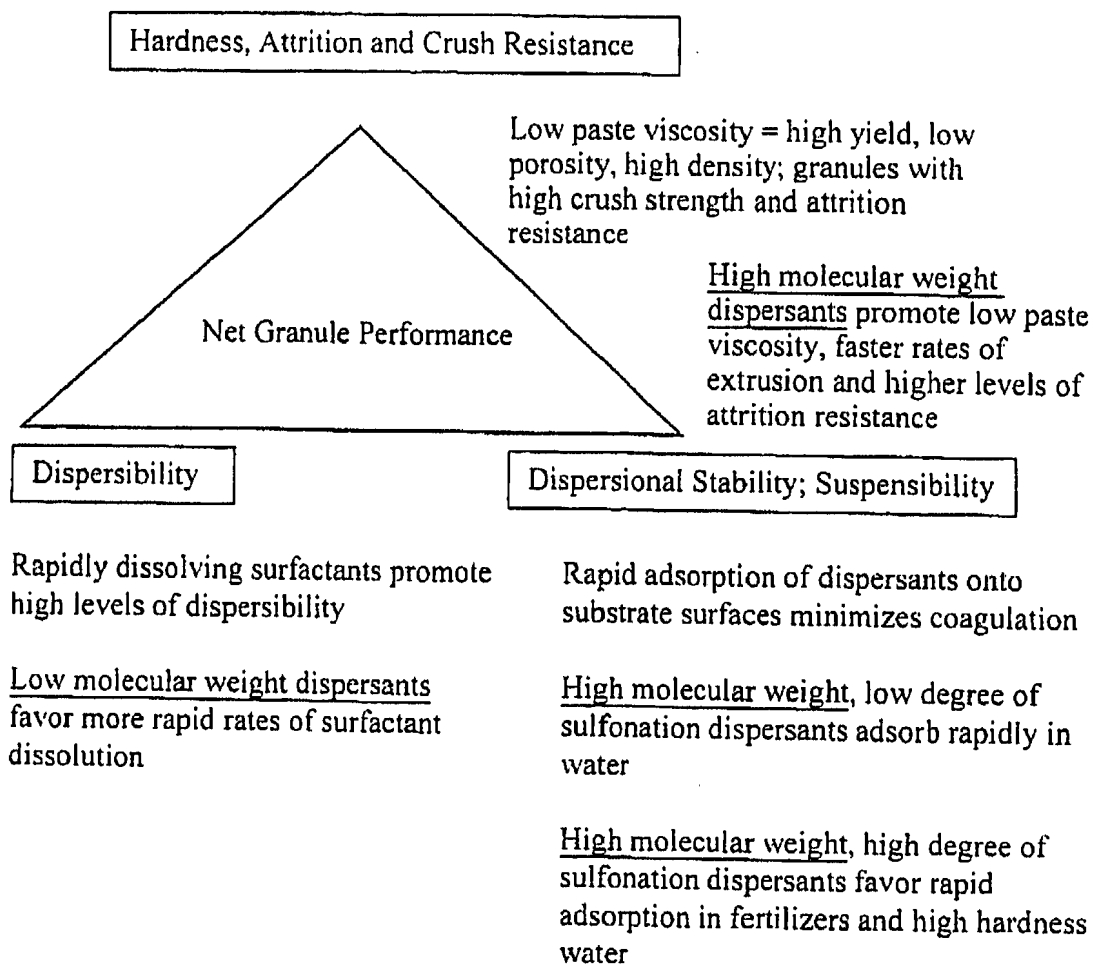


Figure 1 – Dispersant Molecular Weight and Its Influence on Extruded WDGs

The performance variables are hardness which includes attrition resistance and crush strength, dispersibility or the speed and completeness of the disintegration process, and dispersional stability or the ability of a dispersion to resist agglomeration by either coagulation or uncontrolled flocculation.

The first parameter, hardness, etc., is a function of both the rheology of the pastes and the intrinsic pore structure of the agglomerated surfactant system within the formulation. Interestingly enough, the rheology of the paste and the surfactant system are also influences on the manufacturing process, as described by Benbow and Blackburn (1981).

The remaining two, namely dispersibility and dispersional stability, are related to the rates of dissolution of the dispersant and its kinetics of adsorption respectively. These, in turn, are a consequence of interfacial activity which is very heavily influenced by molecular weight. Rate of dissolution varies inversely with molecular weight, and adsorption, directly with molecular weight.

Experimental

Rates of extrusion were determined by collecting and weighing the total amount of paste extruded by an LCI³ bench top extruder in a predetermined period of time. To insure constant feed rates, the feed ram was weighted with a known weight of stainless steel shot.

Rates of surfactant dissolution were determined by forming a tablet from a predetermined amount of surfactant in a Carver press. The tablets were immersed in 342 ppm water and weight loss as a function of immersion time were recorded.

Adsorption isotherms were determined by exposing a known weight of finely milled technical pesticide to a dilute solution of the dispersant in question. Concentration changes of dispersant as a function of time and/or concentration were determined by ultraviolet spectroscopy at $\lambda = 280$ nm as described by Eicke and Dilling (1988).

Ultra low shear rheology was observed and recorded with a Haake⁴ RS 150 CS Rheometer.

Porosity measurements were made with a Micromeretics⁵ 9430 mercury porosimeter.

All other test methods are identical to those described earlier.⁶

Results and Discussions

Hardness and Porosity

Two series of dispersants were prepared for subsequent extrusion into WDGs with chlorothalonil. These dispersants were based on low (0.8 moles/kg) and high (2.9 moles/kg) degrees of sulfonation. The distinguishing characteristic within each series was an approximate 3 fold change in $\bar{M}_{z+1}$, the $z+1$ average molecular weight of each dispersant. Data are described in Tables 1 and 1A.

Series A-C, based upon a low degree of sulfonation showed a variation in $\bar{M}_{z+1}$ from 177 000 to 68 010 and an extrusion rate of 280-140 g/hr. Series D-F based on a high degree of sulfonation showed $\bar{M}_{z+1}$ range from 68 160 to 19 360 and an extrusion rate varying from 320 g/hr to under 240 g/hr. The third column in Table 1, P the Polydispersity, is the ratio of $\bar{M}_{z+1}$ to $\bar{M}_w$ the weight average molecular weight and unlike the traditional way of calculating P , the ratio of the weight average molecular weight, $\bar{M}_w$, to $\bar{M}_n$ the number average molecular weight. In the present work, " P " is used as a relative

³ LCI Corp., Charlotte, NC.

⁴ Haake, Paramus, NJ.

⁵ Micromeretics Inc., Atlanta, GA.

⁶ Dispersions V2 #2, published by Westvaco Corporation, Charleston, SC. pp 2-4.

measure of the molecular weight spread from the center of mass of the distribution to its high end.

Table 1 - Dispersant Molecular Weight and Extrusion Paste Flow

Dispersant	$\bar{M}_{z+1}$	Paste Flow (g/hr)	P ($\bar{M}_{z+1}/\bar{M}_w$)
A	177 000	280	72
B	86 370	240	39
C	68 010	140	17
D	68 160	320	39
E	39 690	>240	17
F	19 360	<240	13

A-C Lignin Degree of Sulfonation = 0.8 moles/kg

D-F Lignin Degree of Sulfonation = 2.9 moles/kg

Table 1 data also show that for both series A-C and D-F, extrusion rates vary directly with $\bar{M}_{z+1}$ and P. $\bar{M}_{z+1}$ is the fourth moment arm around the center of mass of a distribution of individual units or molecules. It is the molecular weight average measured experimentally by hydrodynamic techniques such as sedimentation and diffusion techniques. It can also be calculated from gel permeation chromatographic data as was done in the present case. In the present work, it is being used to signify the presence or absence of a high molecular weight fraction within a distribution of molecules, relative to the mean molecular weight usually represented by $\bar{M}_w$, the weight average molecular weight (Tanford, 1963). The observed performance is believed to occur as a result of clustering of dispersant molecules into large agglomerates with the larger molecules acting as the centers of the clusters. These very large clusters, represented by $\bar{M}_{z+1}$, which are believed to function sterically rather than coulombically (electrostatically), keep particles within the paste further apart than smaller ones would. The greater interparticle distance will result in less particle/particle interaction and subsequently less resistance to flow. The end result is an increase flow rate through the extruder with larger dispersant molecules.

Additional data are listed in Table 1A where porosity, granule density, attrition and the viscosity of the surfactant solution at 0.01 sec^{-1} , a very low rate of shear which approximates self leveling or flow of droplets or pockets of liquid across surfaces and into pores.

It is at this point where a dichotomy appears to develop. Series A shows a *decrease* in porosity, *increase* in density and *decrease* in attrition as extrusion flow rate decreases.

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On the other hand, the opposite is noted with Series B, based on the highly sulfonated lignin. As extrusion flow decreases, porosity, density and attrition resistance increase. The reason for the duality of the response found here may lie with the viscosity of the surfactant system itself which in a freshly extruded paste is in the form of a highly concentrated solution.

Looking at a typical extrusion paste/process response, it is not difficult to envision compressive forces which cause the material to flow and at the point of passage through the compression zone of the extruder lose void volume or porosity. However, immediately after passage through the screen, the extruded paste which is usually a more elastic rather than a viscous system expands in a phenomenon called "dye plate expansion." As this occurs, some pore structure immediately reopens. At this point, the water in the paste which contains relatively high concentrations of dissolved surfactant is free to flow into these openings: *Provided of course its resistance to flow (viscosity) is not too high.* This may be considered somewhat analogous to the self leveling of a coating on a solid surface; a process which is associated with shear rates of 0.01 s⁻¹ or lower.

At this point, the viscosity of the dissolved surfactant system a $\bar{M}_w$ dependant parameter was measured at 50% solids and T=35°C. The data are listed under η in Table 1A.

Table 1A - Dispersant Molecular Weight, Dispersant Rheology and Extrusion Paste Flow

Dispersant	$\bar{M}_{z+1}$	Paste Flow (g/hr.)	$\frac{P}{\bar{M}_{z+1}}$ $\frac{Mn}{Mn}$	Porosity (%)	Density (g/cm ³)	Attrition (%)	* η @ $\dot{\gamma} = 0.01 \text{ s}^{-1}$ @ 35°C
A	170 000	280	72	23.6	1.382	24	∞
B	86 370	240	39	13.4	1.431	8	41×10^6
C	68 010	140	17	10.2	1.502	4	25×10^6
D	68 160	320	39	13.4	1.541	5	7×10^3
E	39 690	240	17	15.1	1.496	5	27×10^3
F	19 360	<240	13	20.2	1.338	8	13×10^6

* η - Viscosity of the surfactant solution at $\dot{\gamma} = 0.01 \text{ s}^{-1}$

They show for the low degree of sulfonation series of dispersants A-C, the viscosity values range from apparent infinity with the highest molecular weight dispersant, "A", to $25 \times 10^6 \text{ mpa}\cdot\text{s}$ for the lowest, "C." In the case of the high degree of sulfonation series, D-F, the viscosities as expected are lower. However, in both cases, as the surfactant viscosity decreases in the low shear post compression region of the process, residual pore structure decreases. Additionally, as density decreases, attrition increases. "It is not

entirely unreasonable to establish the hypothesis that dispersant flow into the post compression or dye plate expansion renascent pore structure of a granule" is a major influence on the residual porosity of an extruded WDG as well as the hardness of the granules and their densities as well.

Dispersibility

Molecular weight also plays a role in the dispersibility of granules. The data in Table 2 describe the result of a number of experiments with a third series of dispersants, numbered 1-4. Here dispersants were used both as supplied and after being ultrafiltered to remove excess inorganic salts such as Sodium Sulfite (Na_2SO_3) and Sodium Sulfate (Na_2SO_4). This process was carried out in a manner to have minimal influence on the molecular weight of the dispersant.

Additionally, the weight average molecular weight $\bar{M}_w$ was the variable of choice here since the working hypothesis is the relationship between bulk dissolution of the surfactant system and granule disintegration. As implied above, dispersant salt content was considered a secondary variable.

The data in Table 2 show a trend. As weight average molecular weight increases, from 2900 to 10 700, the number of inversions necessary to achieve apparent disintegration in 5°C water with a 1000 ppm hardness level, increased from 9-31 in the dispersant series used as supplied. As expected, removal of the excess inorganic salt caused the dispersibility to decrease. However, the trend with molecular weight remained the same. It is worth noting also, that dispersants 2 and 3, while they are two different sulfonated lignin dispersants, their weight average molecular weights cannot be considered significantly different, nor can their salt contents. However, their $z+1$ average molecular weights do differ; 19 360 for dispersant #2 and 276 000 for #3. This observation is also consistent with observations which identify $\bar{M}_{z+1}$ as an important rheological parameter in concentrated systems but a relatively minor one with respect to other bulk properties such as rate of dissolution.

Table 2 - Molecular Weight Effects on Disintegration of Chlorothalonil 80% Extruded WDGs

Dispersant	$\bar{M}_w$	Dispersant Salt Content (%)		Dispersibility*** (# Inversions)	
1	2900*	3600**	23*	2.3**	9*
2	4800	5100	5.8	2.0	16
3	4600	5150	6.0	2.1	16
4	10 700	11 500	2.8	2.0	31

* Dispersant used as supplied.

** Dispersant was ultrafiltered to remove excess inorganic salt.

*** T = 5°C in 1000 ppm hard water.

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Figures 2 and 3 show the result of tablet dissolution studies carried out on the dispersant in the current series. The data are listed in Table 3. Comparison of these data with dispersibility values from Table 2 support the hypothesis that molecular weight and its well documented influence on dissolution exerts the same level of influence on granule disintegration. For example, comparison of the slopes of tangents to the dissolution curves @ $t = 0.5$ min. vary from 14%/min to 2%/min for the dispersants used as supplied and 11.6% to 1.7% for their desalted counterparts. These numbers can be considered the rates of dissolution of the surfactant systems under the conditions of the experiment,

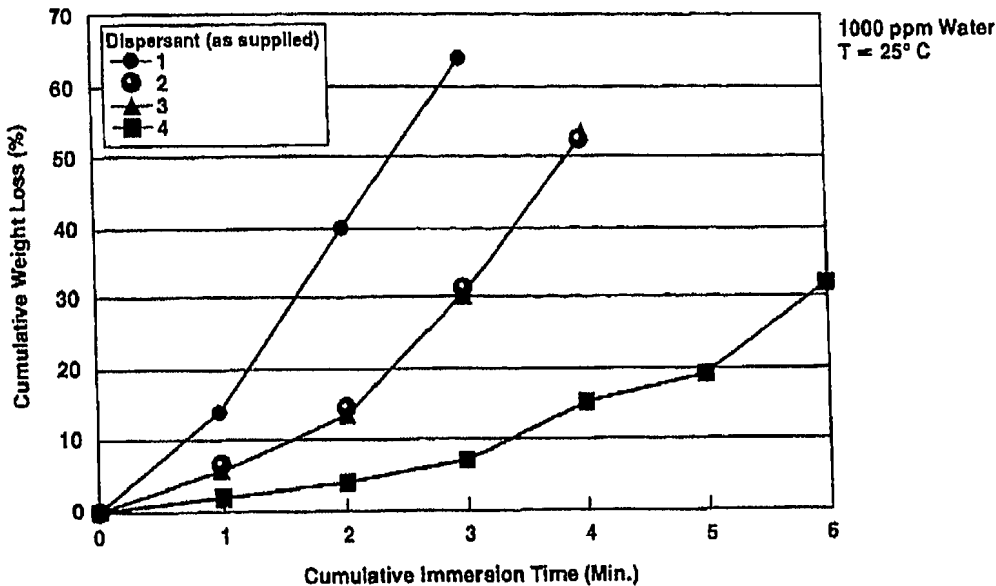


Figure 2 - Dispersant Dissolution

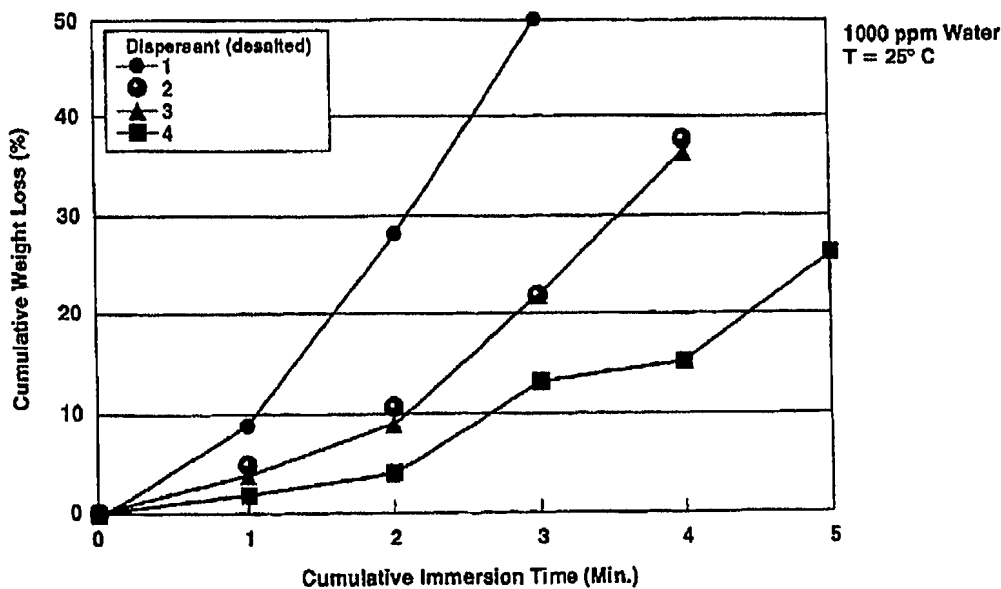


Figure 3 - Dispersant Dissolution

Table 3 - *Dispersant Dissolution Characteristics*

Dispersant	Inversion Time (min)	% Weight Loss (as supplied)	% Weight Loss (desalted)
1 Limiting slope @ $t = 0.5$ min. = 14.5%/min (as supplied) 11.6%/min (desalted)	1	14	9
	2	40	28
	3	64	50
	4	-	-
2 Limiting slope @ $t = 0.5$ min. = 6.25%/min (as supplied) 5.0%/min (desalted)	1	7	5
	2	15	11
	3	30.8	22
	4	51.7	38
3 Limiting slope @ $t = 0.5$ min. = 6.25%/min (as supplied) 4.1%/min (desalted)	1	5.5	4
	2	13.7	9.3
	3	29.5	22
	4	53	36
4 Limiting slope @ $t = 0.5$ min. = 2%/min (as supplied) 1.7%/min (desalted)	1	2	2
	2	4	4
	3	7	8
	4	15	13
	5	19	15
	6	32	26

Dispersional Stability

The third leg of the WDG performance triad is dispersional stability, particularly under the dilute conditions of a spray tank. Here the mechanism of stabilization is coulombic repulsion. However, before this process can occur, adsorption of the dispersant onto the substrate surface must occur. This "primary" or first process is also strongly influenced by molecular weight.

To demonstrate this effect, the adsorption of two dispersants referred to as 5 and 6 onto two substrates, diuron⁷ and atrazine⁸, was measured. Dispersants 5 and 6 are both

⁷ Ex DuPont, Wilmington, DE.

⁸ Ex Novartis, Greensboro, NC.

highly sulfonated kraft lignins with degrees of sulfonation of approximately 3 moles of sulfonic acid groups (sodium salt)/kg. Compound 5 has a weight average molecular weight of 3100 and a $\bar{M}_{z+1}$ average molecular weight of 33 000 while 6 has a $\bar{M}_w$ of 4 400 and a $\bar{M}_{z+1}$ of 250 000.

Table 4 lists the amount of lignosulfonate adsorbed as a function of the total lignosulfonate concentration to which the substrate was exposed. The data do show small but significant differences in the adsorption between the two dispersants in each "technical."

A second experiment designed to test the effect of adsorption difference on dispersional stability was performed. This involved titration of suspension of both diuron and atrazine which had been equilibrated with dispersants 5 and 6 with 1×10^{-3} M lanthanum nitrate. In each case, the suspension stabilized with the more strongly adsorbing dispersant 6 required between 15 and 18% more lanthanum nitrate solution for coagulation to occur.

Table 4 - Lignosulfonate Adsorption

Dispersant 5:	Mw = 3100
	Mz+1 = 3300
	Degree of Sulfonation = 2.9 moles/kg
	Salt Content = 5.8%
Dispersant 6:	Mw = 4400
	Mz+1 = 250 000
	Degree of Sulfonation = 2.9 moles/kg
	Salt Content = 6.0%
Lignin Content (in solution)	Amount Adsorbed at Equilibrium
	(mg Dispersant/g Substrate)
mg/l	at pH = 7
	Diuron
	Dispersant 5 ^a
	Dispersant 6
200	0.4
400	0.8
800	1.0
	Atrazine
200	0.6
400	1.0
800	1.8

^a Data for dispersant 5 supplied by Prof. H. F. Eicke, Institut für Physikalische Chemie des Universität Basel, Private Communication October 9, 1991.

This observation supports the hypothesis that, all other factors being equal, adsorption is favored by higher molecular weight dispersants. Increased adsorption in turn promotes higher levels of dispersion stability, relative to coagulation.

Conclusion

The work presented in the preceding paragraphs has shown that the molecular weight of materials used as dispersing agents plays an important role in influencing the properties of extruded water dispersible granules. It also influences the process of extrusion itself.

It is important to note, however, that polymeric dispersants can be described by several different molecular weight averages. The most common are the number average ($\bar{M}_n$), weight average ($\bar{M}_w$), the z average ($\bar{M}_z$) and the z+1 average ($\bar{M}_{z+1}$) molecular weights. It has become common practice to use the weight average because of its proximate location at the center of mass of a Gaussian distribution of molecular weights. In the case of bulk properties such as the rate of dissolution of a polyelectrolyte such as a lignosulfonate or its absolute solubility, it correlates well with observed formulation and/or surfactant behavior.

Both the weight and z+1 average molecular weights correlate with adsorption. However, it must be stated that all other factors such as degree of sulfonation or ionic character and inorganic salt contents of polyelectrolytes must be equal for a direct correlation between molecular weight and adsorption. In the absence of these data, molecular weight should be used to predict trends only.

When evaluating rheological functions such as paste extrusion, paste flow, or suspension and solution viscosities, it is strongly recommended that one of the higher molecular weight averages, particularly the z+1 average molecular weight be used to guide the work or to predict trends for future experimentation, in addition to the mean or weight average molecular weight, $\bar{M}_w$. In this work, one is dealing with a distribution of fully hydrated agglomerates of molecules whose effective size is determined both by the size of the molecules themselves and by their layers of bound water of hydration as well. The higher molecular weight averages such as $\bar{M}_{z+1}$ reflect the actual species responsible, at least in part, for the observed phenomena.

Based upon the data presented in the preceding paragraphs, several trends have been shown to be molecular weight influenced. These are summarized in Table 5.

With both weight average and z+1 average molecular weight data available and well-designed statistically monitored initial screening studies, used for range finding, subsequent experimentation can be focused on specific properties and formulation development will become both a more predictive and shorter-term effort.

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Table 5 - *Property Trends and Molecular Weight Influence*

Property	Dependance on Molecular Weight	Mw Average
Extrusion Rate	Flow increases with increased molecular weight	$\bar{M}_{z+1}$
Ultra Low Shear Paste Rheology	Viscosity decreases with increased molecular weight	$\bar{M}_{z+1}$
Solution Viscosity at High Concentration	Viscosity at lower shear rates increases with increase in molecular weight	$\bar{M}_w$ and $\bar{M}_{z+1}$ (primary) (secondary)
Dispersant Dissolution	Rate of dissolution increases with decrease in molecular weight and increase in salt content	$\bar{M}_w$
Dispersant Adsorption	Adsorption increases as molecular weight increases	$\bar{M}_w$ and $\bar{M}_{z+1}$ (primary) (secondary)

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Pesticide Formulations and Delivery Systems: Meeting the Challenges of the Current Crop Protection Industry

R. A. Downer, J. C. Mueninghoff, and G. C. Volgas, editors

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Improved Efficacy of Lignosulfonate Dispersants Through a Novel Combination

Reference: Winowski, T. S., Brzezinski, J., and Lebo, S. E., "Improved Efficacy of Lignosulfonate Dispersants Through a Novel Combination," *Pesticide Formulations and Delivery Systems: Meeting the Challenges of the Current Crop Protection Industry*, ASTM STP 1430, R. A. Downer, J. C. Mueninghoff and G. C. Volgas, Eds., American Society for Testing and Materials International, West Conshohocken, PA, 2003.

Abstract: This investigation describes the effect of a combination of lignosulfonate (LS) originating from the sulfite process with an unsulfonated kraft lignin (KL), such that the LS portion provides solubility while the KL provides a hydrophobic region that will strongly adsorb onto the substrate. For reference purposes, previous technologies for the preparation of agricultural dispersants have been included, namely, LS modified by oxidative desulfonation (LS-Ox) and by mild depolymerization/desulfonation (LS-U), as well as commercially available sulfonated kraft lignin (SKL).

Studies were conducted in several formulations including atrazine wettable powder (WP), copper oxychloride (COC) WP, COC extruded water dispersible granules (WDG), and sulfur suspension concentrate. The lignosulfonate/kraft combination (LS-KL) showed a unique ability to maintain suspensibility in extra hard water where the other sulfonated lignins failed. For example, suspensibilities achieved with 2% dispersant in COC WP in extra-hard water at 22 °C were as follows: LS, 40%; SKL, 59%; and LS-KL, 84%.

Keywords: sulfonated lignin, lignosulfonate, kraft, suspensibility, hard water

Introduction

Sulfonated lignins (SL) have a long history of effective use as dispersants, grinding aids, and binders for agricultural chemicals (McCarthy and Islam, 1999). Because they are forest products they are also positively perceived as being safe and renewable. In nature, lignin binds cellulose fibers together to give the trees strength. Lignin must be dissolved to free cellulose for papermaking. Two different processes, sulfite and kraft, are the source of most commercial SLs today. The sulfite process breaks lignin into relatively large pieces and renders them soluble by adding sulfonic groups. The kraft process breaks the lignin into smaller pieces soluble only at high pH. An additional sulfonation step is required to produce effective dispersants from kraft lignin. The starting units of sulfite and kraft lignins differ significantly in size and chemistry. Both of these starting materials are currently being chemically modified to alter their performance properties to meet specific commercial end uses (Lin and Lebo, 1995).

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Sulfonated lignins are particularly useful for dispersing hydrophobic materials. Without dispersing agents small particles quickly agglomerate, increasing their size and sedimentation rate. Sulfonated lignins contain both hydrophilic and hydrophobic regions. The sulfonic, phenolic, and carboxylic groups are hydrophilic and provide water solubility. The aromatic carbon backbone of the lignin is hydrophobic and is attracted to other hydrophobes such as the active ingredient to be dispersed. The more hydrophobic the SL, the more strongly it will adsorb onto the dispersed particle. As the SL adsorbs it increases the particle's Zeta potential, stabilizing the dispersion through electrostatic repulsion (Humphrey and Jensen, 1995). A good dispersant must have the appropriate balance between its adsorbing hydrophobic groups and its hydrophilic components. Furthermore, the balance can be shifted by the nature of the active, pH, water hardness, and temperature. This need for balance under different circumstances is the force that drives chemical modification of the basic lignin materials.

This study compares five different sulfonated lignins. The first is a softwood lignosulfonate (LS) of sulfite origin. It can be considered as the basic starting material for three of the other test lignins in this study. It is relatively large and highly sulfonated. Mild desulfonation of LS makes a second product (LS-U) that is more hydrophobic with better adsorption properties. Oxidation of LS leads to a third derivative (LS-Ox) that has more carboxylic groups and is partially desulfonated. Testing by high pressure exclusion chromatography (HPSEC) shows LS-Ox elutes later and in a tighter grouping than the original LS (Figure 1), indicating it is smaller and less polydispersed (Gargulak, 1997). Desulfonation increases adsorption while smaller size and carboxylic groups maintain good solubility. The fourth derivative is a condensation product of SL and KL. The result is a new product (LS-KL) that is believed to have a heterogeneous structure; the LS portion provides the solubility and the electrostatic repulsion while the unsulfonated kraft

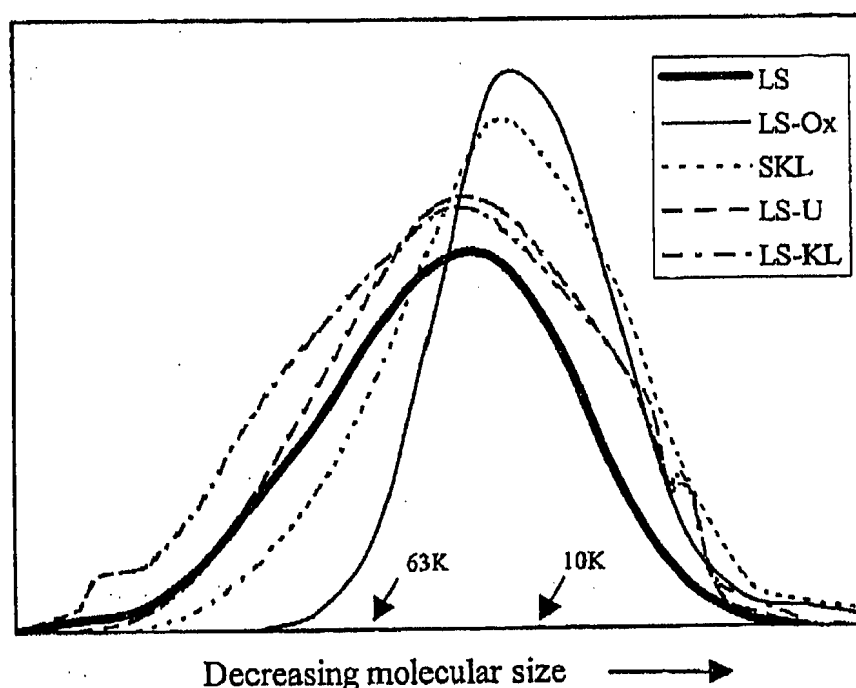


Figure 1 - HPSEC Curves

portion is expected to adsorb strongly to hydrophobic substrates. The LS-KL is the only derivative of LS in this study that has a higher average molecular size. A fifth treatment of sulfonated kraft lignin (SKL) was included as a positive control. Chemistry of the five treatments is listed in Table 1.

Experimental Method

Preparation of Test Formulations

Wettable Powders – Atrazine was mixed with other formulants as follows: atrazine, 80%; dispersant, 2%; Supragil WP wetting agent, 3%; kaolin clay, 15%. The COC formulation was: COC, 85%; test dispersant, variable with 10% maximum; Rhodical wetting agent, 2%; kaolin clay added to make 100%. In every case the mixtures were ground for 5 seconds on a Tekmar A-10 mill and allowed to sit overnight.

Water Dispersible Granules – COC granules were prepared on an LCI Benchtop Basket Extruder. One hundred grams of dry formulation and 36 grams water were combined and blended with a planetary mixer for approximately 30 seconds. The mix was then extruded through a 1mm screen. Moisture of the extrudate was determined immediately on a Cenco moisture balance. A fluid bed dryer with a 40°C airstream was used to reduce total moisture content of the extrudate to less than 1%. The granules were gently broken over a 16 mesh sieve and the -16 + 50 mesh fraction collected. Moisture of the dried granules was determined by Cenco.

Table 1 – Analyses of Test Dispersants

Product	pH, 10% Solution	Carboxyl ¹		Phenolic ²	
		Sodium	-COOH	-OH	Degree of Sulfonation ³
		Weight %, dry basis			
LS: Ultrafiltered Lignosulfonate	8.6	7.0	3.1	2.1	2.2
LS-U: depolymerized desulfonated LS	9.1	8.5	5.2	2.0	1.9
LS-Ox: oxidized desulfonated LS	8.4	8.0	7.4	1.6	0.9
LS-KL: LS and KL condensation product	10.1	9.0	5.2	2.1	1.6
SKL: Sulfonated kraft lignin	10.5	9.3	4.9	1.9	1.3

¹ Weak acid content is calculated as % COO⁻ via pH titration with p-hydroxybenzoic acid addition to assist in endpoint determination.

² Differential UV spectra in alkaline and acidic solution. Aaulin-Erdtman, Svensk Papperst. 57 (1954) 745-760.

³ Moles of sulfonic sulfur per 1000 g of sodium (or calcium) lignosulfonate.

Suspension Concentrates – Liquids were weighed together first and placed in a Waring blender. Dispersant and wetting agents were then weighed and sifted into the liquid with the blender running at low speed. The resulting solution was transferred to the chamber of a Type SV Szegvari Attritor. Sulfur was added on top of the liquid, the attrition mill was turned on slow speed, and 350 mL of 2 mm glass beads were added. Mill speed was then increased to 850 r.p.m.. Temperature held constant at 22 °C with a circulating water bath. Milling was stopped at 60 minutes and the glass beads were separated from the SC by suction filtration. The resulting SC was stored in glass jars at room temperature.

Test Methods

Suspensibility – Suspensibility was measured based on ASTM Test Method for Percent Suspensibility (E 1673-96). Forty mL of test water was placed in a beaker and 4.00 g (W_1) of WP was added onto the surface of the water and allowed to stand for 30 seconds to observe wetting. The mixture was then stirred for 90 seconds and transferred quantitatively to a suspensibility cylinder. Tests were usually done at 22 °C. Testing at 5 °C and 30 °C was done in a water bath; make-up water was pre-adjusted to temperature. Water was added to the cylinder to take the level to 250 mL. The cylinder was then inverted 15 times and allowed to stand undisturbed. Exactly 30 minutes later the top 225 mL were removed from the cylinder by vacuum. The bottom 25 mL were transferred quantitatively to a weigh boat and dried to a constant weight (W_2). Suspensibility was calculated as:

$$\% \text{ Suspensibility} = 111 * (W_1 - W_2) / W_1 \quad (1)$$

Suspensibility of WDG was measured as above except wetting time was not observed. Suspension concentrates were treated as described above except approximately 7.0 g of wet SC was weighed and multiplied by the percentage dry matter to calculate W_1 .

Resuspensibility – Suspensions were prepared as described above but were allowed to stand overnight. Resuspensibility was measured as the number of complete inversions (upside down and back) required to loosen all the sediment from the bottom of the cylinder.

Attrition – Three grams (W_3) of the granules were placed in a cylinder ($\ell = 95$ mm, $r = 25$ mm) containing fourteen 12.5 mm and one hundred twenty-five 6.4 mm ball bearings. After rotating for 2 minutes at 25 r.p.m. the granules were collected and the +50 mesh portion weighed (W_4). Durability was calculated as:

$$\text{Durability} = (W_4 / W_3) * 100 \quad (2)$$

Viscosity – Viscosity was measured on a Brookfield R.T.V.. Testing was done immediately after milling. Readings were taken at 10, 20, 50, 20, and 10 r.p.m. with one minute intervals between each reading. The two 20 r.p.m. readings were averaged and recorded as the viscosity in this study.

Results and Discussion

Atrazine WP

Suspensibility of atrazine was poor without the addition of dispersant (Table 2). Adding LS in hard water improved suspensibility somewhat, but the four enhanced treatments with lower degrees of sulfonation were significantly more effective. There appears to be an inverse correlation between degree of sulfonation and suspensibility in extra-hard water, with LS-KL as a possible outlier. LS-KL is believed to be heterogenous. It is likely that it presents a very hydrophobic portion to adsorb onto the atrazine particle. Increasing water hardness may cause a reconfiguration of the LS molecule in which more of the hydrophobic components fold to the interior, with the proportion of sulfonic groups increasing on the surface. This would render the dispersant less adsorbant and more water soluble. LS and LS-U were strongly affected by extra-hard water. SKL and LS-Ox were less affected; this may be due both to their smaller size and lower degree of sulfonation, which could reduce the potential for reconfiguration. LS-KL is larger than LS and has an intermediate degree of sulfonation. It may retain its ability as a dispersant because the KL portion remains on the surface as a adsorbant hydrophobe.

Table 2 - Atrazine WP with 2% dispersant

2% Dispers- ant,	Deg. of Sulfon- ation	Suspensibility, %		Resuspensibility, # of inversions	
		Hardness, ppm		Hardness, ppm	
		342	1000	342	1000
Control	NA	38	34	1	1
LS	2.2	52	24	1	1
LS-U	1.9	90	38	5	1
SKL	1.3	92	85	23	1
LS-Ox	0.9	91	89	7	2
LS-KL	1.6	92	90	NA	NA

Copper Oxychloride WP

Copper oxychloride was investigated first as a wettable powder. Evaluation of suspensibility in soft water (34 ppm) revealed that all five dispersant treatments were very effective. Increasing water hardness reduced suspensibility in the same manner as previously seen with atrazine (Table 3). The effect was even more dramatic as water temperature increased. Increasing the temperature of the system causes more molecules of dispersant to have sufficient thermal energy to break the hydrophobic attraction and desorb from the COC (Tamamushi, 1963). Maintenance of suspensibility by LS-KL suggests that this heterogeneous molecule adsorbs more strongly than the more homogeneous LS or SKL.

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Table 3 – *Suspensibility of COC WP with 2% dispersant in varied water conditions.*

	Hardness	Temperature		
		5 °C	22 °C	30 °C
LS	34 ppm	94	93	92
	342 ppm	92	80	83
	1000 ppm	54	40	19
SKL	34 ppm	94	92	91
	342 ppm	93	93	89
	1000 ppm	86	59	46
LS-KL	34 ppm	94	93	90
	342 ppm	93	92	89
	1000 ppm	88	84	77

It was noted with atrazine that resuspensibility became more difficult as suspensibility improved (Table 2). It was confirmed with COC that suspensibility greater than 90% was associated with poor resuspensibility (Figure 2). For this reason, a target of 85% suspensibility was set and the level of dispersant adjusted accordingly (Table 4). The least expensive (assuming cost correlates to level of processing) dispersant to purchase might be the most expensive one to use; five times as much LS was required to achieve the same level of performance as its daughter products. LS-KL once again showed better performance in extra-hard water.

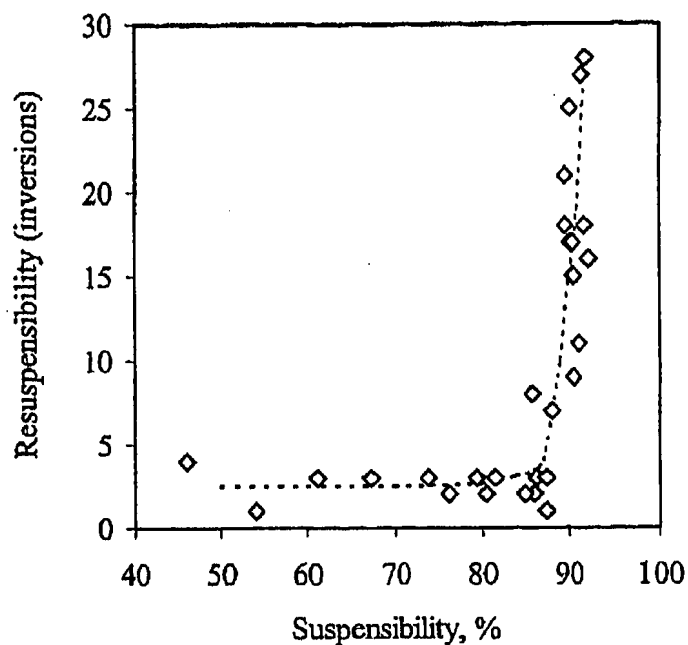


Figure 2 - *Optimum suspensibility of COC WP*

Table 4 ~ Dispersant required to achieve 85% suspensibility of COC-WP

Dispersant	Deg. of Sulfonation	Dispersant needed, %	
		342 ppm	1000 ppm
LS	2.2	4.0	>10
LS-U	1.9	0.7	9.6
LS-Ox	0.9	<0.5	6.2
LS-KL	1.6	<0.5	3.5
SKL	1.3	0.8	9.6

Copper Oxychloride WDG

The binding properties of SLs are well utilized in extruded granules. Granulation improves product flow and container emptying, as well as reducing the possibility of inhaling dust (AGROW, 2001). These benefits are lost if the granules revert back to powder during transport. Without SL, durability of the granules was 25% (75% reverted to powder). Addition of 1, 2, and 3.5% SL increased average durability to 74, 87, and 98%, respectively (Table 5).

Table 5 ~ Results with COC Extruded Granules

	Dosage, %	Test Dispersant					Means of all five
		LS	LS-U	LS-Ox	LS-KL	SKL	
Suspensibility in 342 ppm, %	1.0	77	87	91	77	72	80.8
	2.0	89	92	93	89	84	89.4
	3.5	93	94	91	89	87	90.8
Suspensibility in 1000 ppm, %	1.0	19	36	38	50	21	32.8
	2.0	25	66	35	74	35	47.0
	3.5	28	70	36	78	34	49.2
Durability, % (100 - Attrition)	1.0	74	73	73	78	73	74.2
	2.0	88	90	82	85	92	87.4
	3.5	99	98	98	98	96	97.8

No significant difference in binding ability was apparent between the different SLs tested, but there were once again differences in suspensibility. LS-U and LS-Ox were the most effective dispersants in hard water while LS-KL was once again the most effective in extra-hard water. Durability may be the limiting requirement in some extruded granules. It might be necessary to use a higher level of product to bind than is required to disperse. In this situation a less refined SL dispersant might be appropriate.

Sulfur SC

Sulfonated lignins are also proven as grinding aids (Lin and Lebo, 1995). Once again, it is important that the SL adsorb onto the hydrophobic surface of the target particle. The absorbed SL creates a barrier that prevents return to the aggregated state. As the aggregate is broken up into small discrete particles surrounded by SL and its associated solvent layer, freedom of movement increases and viscosity is reduced (Conley, 1996).

The five SLs under study were tested as dispersants in a 6# sulfur suspension concentrate (Table 6). The viscosity reported reflects conditions immediately following milling; it was noted that viscosity dropped significantly after 24 hours. It should also be noted that no thickening agent was used. Viscosity achieved a minimum level with about 2.5% SL and plateaued or increased as more was added. LS-KL and SKL caused the most dramatic reductions in viscosity. It has been reported that viscosity increases with the size of the SL dispersant molecule (Delli Colli, 1986). This was not the case here since LS-KL is the largest molecule and LS-Ox is the smallest.

Table 6 – *Effect of dispersant on wet milled sulfur*

Dosage ¹	Dispersant				
	LS	LS-U	LS-Ox	LS-KL	SKL
Viscosity ² , cps					
1.3 %	2200	2880	1770	700	300
2.5 %	500	1200	930	300	300
3.8 %	600	1210	1180	230	400
5.0 %	810		2040	300	
Suspensibility in hard water, %					
1.3 %	19	55	51	58	69
2.5 %	26	52	53	63	63
3.8 %	45	58	52	62	66
5.0 %	44			71	

¹ Dosage calculated as % dispersant on dry active

² Brookfield R.T.V. at 20 r.p.m.

Conclusion

Combination of lignosulfonate with unsulfonated kraft lignin to form LS-KL is an effective method for enhancing the performance of the lignosulfonate raw material. In addition to a general enhancement of performance properties, the combination provides a unique resistance to the effect of extra-hard water on suspensibility of the formulation.

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