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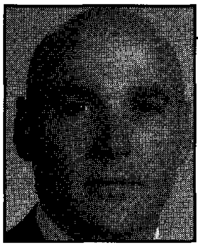
NEW WATER-BASED DEFOAMERS OFFER IMPROVED PERFORMANCE AS WELL AS ENVIRONMENTAL ADVANTAGES

They are free of hydrocarbon oils

BY J.H. WAMSLEY AND T. GAMMON



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WATER-BASED defoamers are defined as products wherein water is the carrier or continuous phase. These products are oil-in-water emulsions and as such are dispersible in water. Typically, water-based defoamers contain from 75 to 90% water.

Water-based defoamers have been used by the pulp and paper industry for many years. The water-based products used in the 1950s and 1960s were called "paste defoamers", and indeed had the consistency of a paste or cold cream.

The rationale to use water-based (paste) defoamers was different in those days than it is today. First, water-based defoamers constituted one of the first types of foam control agents developed for the paper industry. The idea of using fatty triglycerides (fats and oils) to control various types of foam has long been known, and as such was applied to defoaming paper stock. Next, defoamers offered a profitable outlet for excess fatty materials from rendering and fatty oil processing plants. Several of the first defoamer suppliers manufactured or had access to large supplies of various fatty materials and by-products. Finally, there was the cost factor. Water-based emulsions were relatively low in cost for both the producer and the consuming pulp and paper mills where they were found to be effective from a cost/tonne standpoint.

The applications for water-based defoamers were different than they are today. The brownstock or pulp washing defoamers in the 1950s and 1960s were not particularly persistent, and pulp washing was not as efficient as it is now, so that residual foam and entrained air was a major problem in screening, deckering, and bleaching operations. Thus, large quantities of relatively low cost defoamers were needed to remove air and enable this equipment to process pulp at designed or over-designed capacity.

Early paste defoamer formulations were composed of fatty molecules such as sulphated tallow, tallow fatty acid soaps, propylene glycol or glycerine fatty esters, hydrogenated fats, paraffin waxes, and the like. Being paste-like in consistency the products had to be transferred from drums into makedown vessels manually or by using certain types of grease pumps. In the makedown vessels the pastes were diluted to 0.5 to 5.0% emulsions prior to feeding into the mill stock systems.

Problems in the makedown of the paste defoamers were common. The makedown water needed to be warmed as the paste-like products would not disperse in cold water. If the makedown water was too hot (i.e. above 120°F) the fatty components in the defoamer would soften and would have a tendency to agglomerate together so that a useful dispersion would not form. Since the primary emulsifying agents were fatty acid soaps, water hardness also played an important role. If the water was too hard (above 200 parts per million (ppm) total hardness) the soaps could precipitate which would again

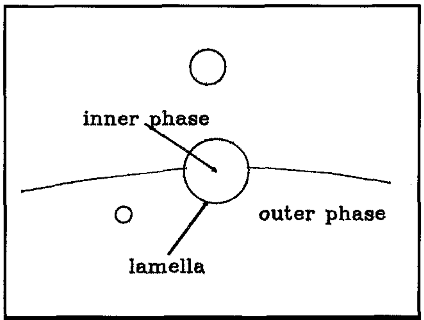


FIG. 1. FOAM PHASES.

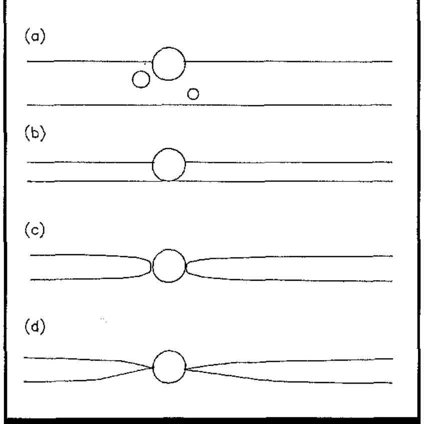


FIG. 2. (A) THE PARTICLES ARE IMMERSED IN A THICK FILM; (B) ORIENTATION JUST PRIOR TO BRIDGING; (C) FILM THINNING ACTION; (D) FILM RUPTURE BY PARTICLE.

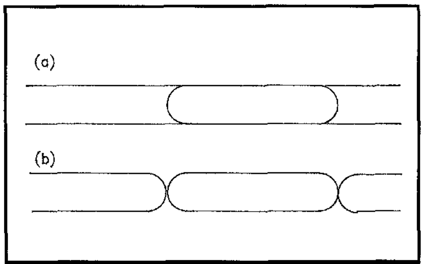


FIG. 3. (A) SURFACTANT ON THE SURFACE OF THE LAMELLA; (B) FILM RUPTURE BY SURFACTANT.

result in agglomeration. If the water was totally soft, foaming in the makedown vessel would occur as well as a distinct reduction in product performance. Finally, feeding the made-down emulsion of these early defoamers frequently presented problems of agglomerates of hard water soaps and waxes clogging screens or wire facings. These deposits could eventually result in a mill shutdown or poor quality finished pulp or paper.

Even with all these many inconveniences and potential problems, water-based paste defoamers continued to be used and actually gained in popularity. In fact, there were several attempts to use these defoamers in bulk quantities. These attempts were never really successful mainly because the natural variation in the fatty materials used in the products (such as degree of saturation, melting point, and solubility) resulted in variation in the consistency of the final products.

The water-based defoamers of today have addressed these and other problems. They are tailored to meet industry needs. They are fluid, pumpable, and remain so over extended periods of time. They do not contribute to mill deposit problems, or dirt count in the finished paper. They do not detract from sheet strength or sizing efficiency. Of greatest importance, these defoamers are free of hydrocarbon oils, and the majority of their components are friendly to the environment and are even considered biodegradable. (OECD Method 301B, EPA Method 796.3260)

FOAM

To have a full understanding of these products there must be a basic knowledge of the defoaming mechanism and the cause of foam itself.

Pure liquids do not foam. The degree of foaminess in impure liquids depends on the quantity and type of contaminants. Contaminants that directly affect the surface tension of the liquid have the tendency to create favorable conditions for foam. In order to discuss the heterogeneous system, certain terms need to be defined. The insoluble gas is referred to as the inner phase. The liquid is the outer phase and these two phases are stabilized by the thin liquid film called the lamella, Fig. 1.

The film has an extraordinary ability to recover from an applied force. This may be explained by the Gibbs Elasticity equation.

$$E = \frac{2dv}{d \ln a}$$

Where:

E is defined as the Gibbs Elasticity;
v is the surface tension;
$\ln a$ is the logarithm of the area of the film.

The ability to recover from an applied force is explained by the definition of E. An applied force to the lamella increases surface tension which draws liquid from the surrounding areas. Since the three phases are in equilibrium with each other the change in surface tension is able to draw upon the liquid phase and stabilize the film to prevent any further degradation of the film.

Another important point is that small bubbles are more stable than large ones. This is explained by the Young-Laplace equation which indicates that the pressure inside a bubble is greater than the external atmospheric pressure.

$$P = 2v\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Where:

P is the pressure difference;
v is the surface tension;
R_1 and R_2 are the radii of curvature.

Further examination of this equation implies that the pressure inside a small bubble is greater than the pressure inside a large bubble since there is more liquid per area of the small bubble to help maintain the equilibrium.

Now how does all of this apply to defoamers? Theoretically, defoaming occurs in two ways. It either occurs by a particle or a surface active agent interfering with the stable lamella. For most aqueous foams the particulate type has

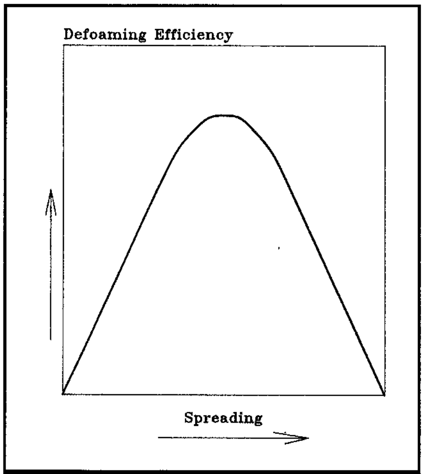


FIG. 4A. OPTIMUM SPREADING IN FOAMING SYSTEM.

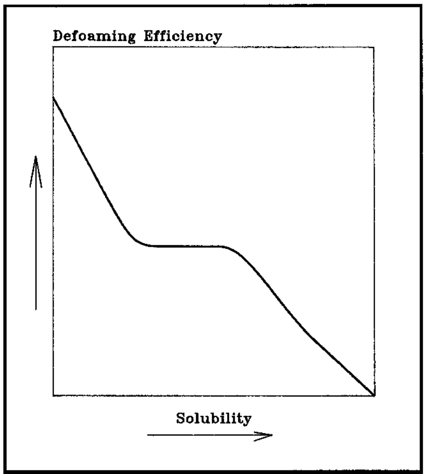


FIG. 4B. OPTIMUM SOLUBILITY IN FOAMING SYSTEM.

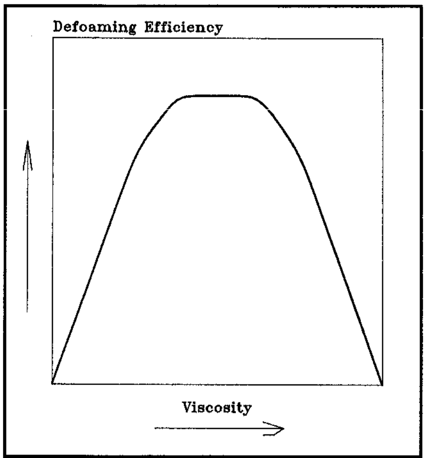


FIG. 5A. OPTIMUM VISCOSITY IN FOAMING SYSTEM.

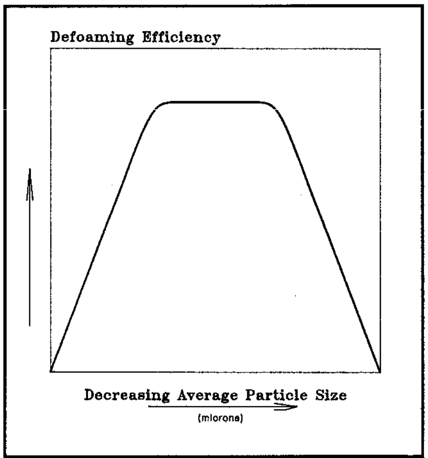


FIG. 5B. OPTIMUM AVERAGE PARTICLE SIZE OF HYDROPHOBIC PARTICLES.

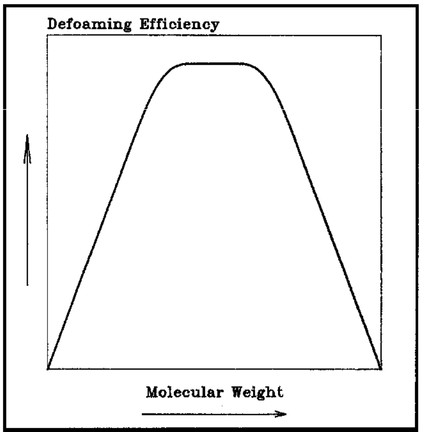


FIG. 6. OPTIMUM MOLECULAR WEIGHT OF ALL DEFOAMER FORMULATION COMPONENTS.

been found to be the most effective.

In the foam, the particles are spread out on the lamella. Since the particles are hydrophobic they push the water away from them creating a weak spot in the film and thus a rupture occurs, Fig. 2.

Surface active agents have the same basic effect on the lamella. Droplets of insoluble liquids such as silicone are spread on the lamella. These droplets form a bridge which is similar to the particle defoaming. The difference in surface tension at the point of contact causes an unstable area in the lamella which leads to rupture, Fig. 3.

Thus several key physical properties are important in the selection of defoamer components, and in the development of final formulations. These are:

Spreading and solubility: As previously discussed these properties dictate how well the defoamer will disperse into the foaming media, how fast it will react, indeed if it will react at all, and if the formulation will be sufficiently persistent to be cost effective, Fig. 4.

Optimum average particle size distribution of hydrophobic particles and viscosity: As indicated particle size is important for the bridging mechanism. If the average particle size is too large, efficiency is poor. A plateau region is then reached. Finally, if the average size of the particles is too small, they are not able to bridge the lamella and little or no defoaming can occur.

Viscosity of the final product is simply a physical property which can have a significant effect on two previously discussed properties; spreading and solubility, Fig. 5.

Optimum molecular weight distribution of components: It is well known that chemical species such as mineral oils, fatty amides, silicone compounds and the like have an optimum molecular weight distribution suitable for the majority of defoaming applications. This molecular weight affects the physical properties of the compound. Cost factors, of course, also play a major role in defining the optimized materials to be used in commercial defoamers, Fig. 6.

Water-based defoamers are emulsions or dispersions of formulated, hydrophobic materials in water. Species of long chain fatty materials have been determined to have the optimum molecular weight distribution, and physical properties (such as solubility and spreading) for use in fluid, pumpable water-based defoamers for pulp and paper systems.

Particle size distribution of the hydrophobic particles dispersed in the water phase is controlled by the chemical nature of the particles, emulsifier type and amount, the manufacturing process temperatures, and milling conditions.

At Rhone-Poulenc Paper Chemicals it has also been determined that the base fatty materials used in water-based defoamers can be modified for improved performance.

The need for improved performance in two distinct areas has been emphasized. These are applications where the environment is higher in temperature, and areas where extremely fast "foam knockdown" is needed.

- Most water-based defoamers which are free of mineral oils, hydrophobic (silicone-treated) silica, and fatty amides (ethylene-bis-stearamides) have an upper limit of efficiency in foaming systems which are higher in temperature than 120 to 130°F.

The reason for this is that these are the temperatures at which many of the fatty components begin to soften or melt resulting in loss of integrity of particle size and shape.

We have found that the fatty materials used in water-based defoamers can be modified through a unique chemical reaction so that particle size and shape are maintained at temperatures up to 150°F or even 160°F, Fig. 7.

When this process is used there are no differences in the physical properties of the final products (viscosity and stability with time) and indeed no chemical difference if the products were to be analyzed.

A difference in the dilute emulsion (i.e. 0.50%) of the products can be noticed with the modified product being slightly more insoluble. The modified product does however disperse readily, and most importantly redisperses easily with only slight agitation.

Case History 1: A 1000-tonne/day integrated bleach kraft mill in the US Mid-Atlantic area was using an oil-containing emulsion-type product for defoaming and decker vat control in the screen room and bleach plant. Product performance was satisfactory. However, pitch outbreaks resulted in frequent final paper rejection due to excess dirt count.

Oil-free, water-based defoamers were evaluated and showed promise. However, due to the mills temperature fluctuation of 120 to 150°F, consistent acceptable performance could not be attained.

After a system analysis and laboratory studies Rhone-Poulenc Paper Chemicals evaluated Fleetcol 9151, a modified oil-

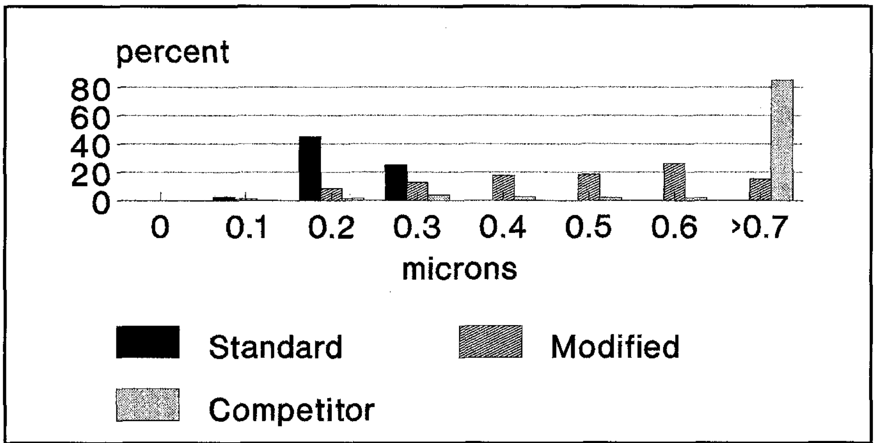
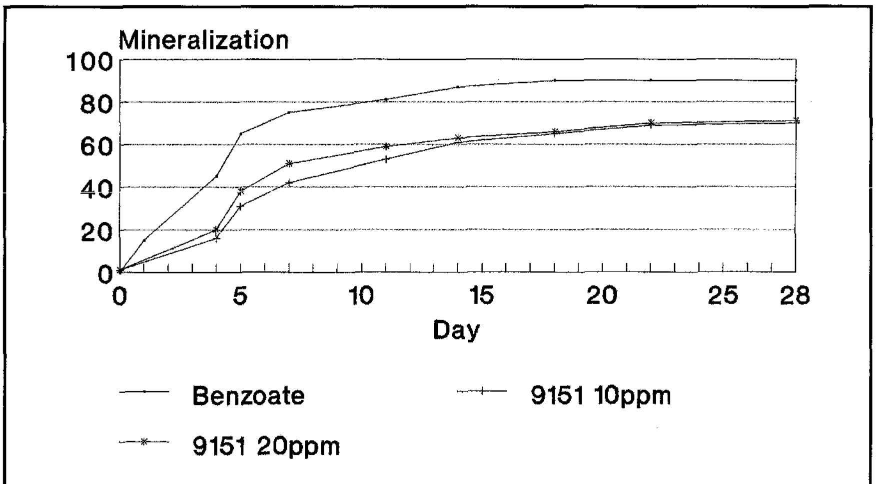


FIG. 7. PARTICLE SIZE DISTRIBUTION STANDARD AND MODIFIED PARTICLES.



OECD Method 301B EPA Method 796.3260

FIG. 8. BIODEGRADATION FLEETCOL 9151.

free, amide-free, silicone-free water-based defoamer which incorporates new proprietary technology for water-based defoamers. The initial mill trials showed extremely good results. Operating temperatures in the mill have even increased as high as 160°F occasionally. The mill has used Fleetcol 9151 for over four years and pitch outbreaks as well as paper rejection are down. An added benefit has been a reduction in the need for defoamer on the paper machines.

Mill description — Mid Atlantic US - Bleached Kraft;
Size — 1500 tonne/day (t/d);
Finished Products — Coated offset, label, rotogravure;
Defoamer — Oil containing water based in screen room and bleach plant;
Problem — Frequent pitch outbreaks — excessive dirt count in finished paper;
Temperature of System —120° - 150°F (variable);
Solution — Fleetcol 9151 (has been used for four years);
Added benefits — Reduction in defoamer usage on paper machines.

A second shortcoming of water-based defoamers is in applications which are not considered severe foaming situations. Typical of these are some pulp and paper mill waste treatment systems. Most mills no longer want mineral oil-based or mineral oil-containing emulsions for this application due to environmental concerns.

While standard oil-free water-based defoamers work well in most waste treatment systems, cost can be higher than is desired. This is because most waste treatment systems are not rich in surfactant-type components which, of course, create the foam. And yet they also serve to help spread or emulsify insoluble defoamer particles into the aqueous medium. The ambient temperatures of most waste treatment systems also reduce this spreading effect.

At Rhone-Poulenc, it has been determined that by modification of the base fatty particles used in our water-based defoamers it is possible to increase their ability to spread in low surfactant, ambient temperature systems.

These modifications are not simply the addition of more emulsifiers which would aid spreading, but would also reduce product performance and persistence.

Case History 2: An 800-t/d bleached kraft mill in the US Northeast was using oil-free water-based defoamers from two suppliers for the waste treatment application. Product performance was acceptable. However, costs were extremely high and tended to increase in the winter months.

Through a system study and on-site laboratory testing, Rhone-Poulenc Paper Chemicals evaluated and recommended Fleetcol 9129, another modified water-based defoamer. Trial results showed that Fleetcol 9129 was a more cost effective defoamer than the two products currently in use. Cost per tonne decreased by more than 35% compared to the previous product. Fleetcol 9129 has been used by this mill for their waste treatment system for more than two years.

TABLE I: PROPERTIES OF TYPICAL WATER-BASED DEFOAMERS.

Appearance — White, fluid, emulsion
Viscosity (Brookfield) — 200-500cps
Stability — 6 months maximum
Composition — free of mineral oil, amide, and silicones
Solubility in water — Readily dispersible
PH (as is) — 8.5 - 9.5
% Solids (Oven) — 10 - 25%
PH Range (of Application) — 3.0 - 10.5
Temperature Range (of Application) — Ambient — 160°F
Conductivity Range (of Application) — 5000 maximum
Method of Addition — Fed directly without dilution

Fleetcol 9129 has been tested and is considered to be biodegradable. (OECD Method 301B).

Mill description — Northeast US —Bleached Kraft;
Size — 800 t/d;
Finished Product(s) — Bond, cover, envelope, ledger, etc.;
Defoamer — Oil-free water-based (two suppliers) in waste treatment system;
Problem — High defoamer cost. Increased in winter;
Solution — Fleetcol 9129 - lower cost (more than 35%), — lower in solids, — biodegradable, — used for two years.

Water-based defoamers have many advantages over oil-based defoamers and can be used in many pulp and paper mill applications. Advantages are focused chiefly around the product's freedom from hydrocarbon oils. These advantages include:

- Negligible contribution to pitch deposits;
- No detrimental effects on sizing efficiency or sheet strength;
- No dioxin precursors;
- Versatility, and cost effectiveness.

Water-based defoamers can be used in pulp screening and bleaching, secondary fibre operations, mechanical pulping, papermaking and waste treatment.

The modifications needed to accomplish this performance improvement have not affected the physical properties or the costs of Rhone-Poulenc water-based defoamers Table I.

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Résumé: L'industrie du papier utilise depuis de nombreuses années des antimousses à base d'eau. Les premiers produits avaient la consistance d'une pâte épaisse. Les variétés subséquentes devinrent fluides et purent être pompées. Cette communication résume l'utilisation des antimousses à base d'eau, avant de mettre l'emphase sur les améliorations récentes apportées par la société Rhone-Poulenc.

Abstract: Water-based defoamers have been used by the paper industry for many years. The first products were paste-like in consistency. Later varieties were fluid and pumpable. This paper reviews water-based utilization briefly and then focuses on recent improvements which have been developed by Rhone-Poulenc.

Reference: WAMSLEY, J.H., GAMMON, T. New water-based defoamers offer improved performance as well as environmental advantages. *Pulp Paper Can* 95(5): T190-193 (May 1995). Paper presented at the 79th Annual Meeting of the Technical Section, CPPA, at Montreal, Quebec, on January 26 to 29, 1993. Not to be reproduced without permission. Manuscript received November 5, 1992. Revised manuscript approved for publication by the Review Panel, December 29, 1993.

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