Gypsum Wallboard Chemical Additives

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Wallboard

Synopsis

Gypsum wallboard consists of a hardened gypsum - containing core surfaced with paper or other fibrous material suitable to receive a coating such as paint. It is common to manufacture gypsum wallboard by placing an aqueous core slurry comprised predominantly of calcined gypsum between two sheets of paper thereby forming a sandwich structure. The aqueous gypsum core slurry is allowed to set or harden by rehydration of the calcined gypsum, usually followed by heat treatment in a dryer to remove excess water.

Conventionally in the manufacture of gypsum board, pre-generated foam is added to the board core slurry mix to decrease the weight of the gypsum board. This foam is generated from a mixture of a liquid foaming agent, air and water in a suitable foam generating apparatus. The foamed gypsum slurry is then deposited upon a moving paper substrate, which, itself, is supported on a long moving belt. A second paper substrate is then applied on top of the slurry to constitute the second face of the gypsum board and the sandwich passes through a forming station, which determines the width and thickness of the gypsum board. In such a continuous operation the gypsum slurry begins to set immediately after passing through the forming station. When sufficient setting has occurred the board is cut into commercially acceptable lengths and then passed into a board dryer. Thereafter, the board is trimmed, bundled, shipped, and stored prior to sale.

The majority of gypsum wallboard is sold in sheets that are four feet wide and eight feet long. The thickness of the sheets varies from about one-quarter inch to about one inch depending upon the particular grade and application, with a thickness of about one-half inch being most common. A variety of sheet sizes and thicknesses of gypsum wallboard are produced for various applications.

Manufacture

- In the manufacture of gypsum wallboard, stucco and a variety of additives are combined with water to form a slurry, which is deposited between paper liners and allowed to harden
- The hardening process occurs through the hydration of calcium sulfate hemihydrate (stucco) to the dihydrate form (gypsum)
- The viscosity of the stucco slurry must be low enough to flow evenly across the paper in the forming section of the manufacturing process

Stucco – Wet End Manufacture

- Gypsum wallboards' major ingredient is calcium sulfate hemihydrate, i.e. stucco. Stucco is manufactured from natural rock or from a synthetic source by:

Drying

- The crude gypsum rock is put through a kiln to remove excess water that was common from the source

Grinding

- This dried rock is ground and pulverized to a desired fineness. There are various types of equipment used in this process. This ground gypsum is commonly referred to as landplaster

Stucco – Dry End Manufacture

Calcination

- The landplaster is passed through a calciner, (i.e., kettle, rotary tubular, roller mill and hammer mill). Each of these calciners perform the same chemical reaction:

$$\underset{\text{Landplaster (gypsum)}}{CaSO_4 \cdot 2H_2O} + \text{heat} \rightarrow \underset{\text{Stucco}}{CaSO_4 \cdot \tfrac{1}{2} H_2O} + \underset{\text{Steam}}{1\tfrac{1}{2} H_2O \uparrow}$$

- The stucco is stored for the production of wallboard

Stucco – Wet End Manufacture

- The reverse of the previous chemical reaction is necessary to re-form the stable form of gypsum, landplaster. When stucco is mixed with water, the following reaction occurs:

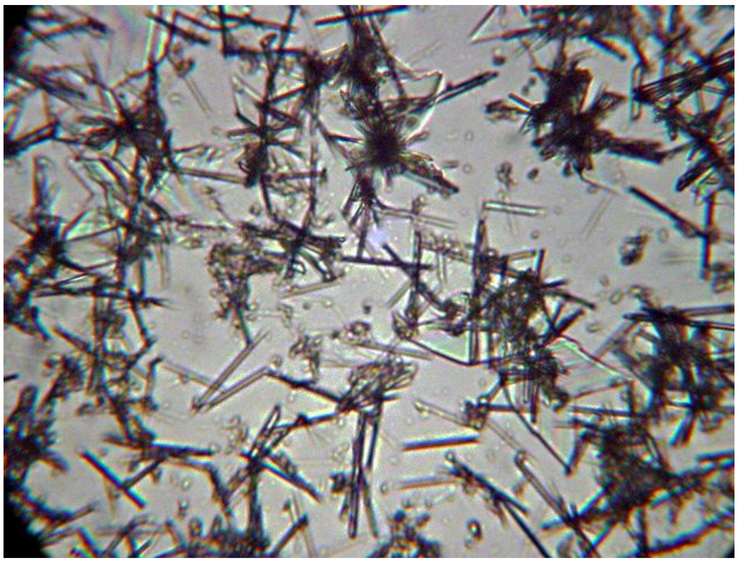
$$\underset{\text{Stucco}}{CaSO_4 \cdot \tfrac{1}{2} H_2O} + \underset{\text{Water}}{1\tfrac{1}{2} H_2O} \rightarrow \underset{\text{Landplaster}}{CaSO_4 \cdot 2H_2O} + \text{heat}$$

- The above reaction is allowed to occur between two sheets of paper, the face or cream, and the back or greyback
- The re-formation of landplaster from stucco is now going to be explored, as well as the effects of chemical additives that are commonly used

Stucco – Solubility

- Stucco is slightly more soluble in water than the landplaster
- In the wet-end mixer, stucco, water, soap and other additives are mixed
- A saturated stucco slurry forms and its dissolution into the water converts it into landplaster
- Landplaster, being less soluble, precipitates out of solution

Stucco – Crystallization – Neat Slurry



- When all the stucco has converted to landplaster, the stucco slurry begins to harden
- Agitation in the mixer influences set time by increasing the stucco solubility
- The setting time of the slurry, as well as the amount of water, has an effect on the <u>size</u> of the gypsum crystals formed
    - Faster setting times and insufficient free water will cause shorter crystals
- Gypsum, unlike cement, is a physical structure rather than a chemical structure. The needle-like gypsum crystals form a network to give the board its physical integrity
- The crystals are closely interwoven, giving the core most of its wet strength. After drying, the frictional forces of these crystals increase the strength of the core. This helps in the handling of the wet board
- Crystal formation should not appreciably begin in the mixer. These crystals will be broken down and thus reduce their length. Further crystal to crystal interactions are thus limited
- If the stucco contains some non-calcined landplaster, then early setting of the slurry can be observed, which can result in problems with the paper/core bonds
    - This can lead to blisters on the paper and splitters on the face and back of the board. If the stucco was over calcined, then similar effects will be observed since sufficient crystal growth is inhibited
- Water demand is sometimes reduced by aging the stucco. This is done by exposing the calcined gypsum to water vapor. This reduces the ability of the stucco to disintegrate on contact with other particles, thus causing increased surface area
    - This has some negative effect on the setting characteristics of the stucco and, as a result, on the strength of the gypsum formed

Paper – Core

- The crystals also interlock with the paper fibers that protrude from the bond liner of the paper, mechanically increasing the paper/core strength
- This interaction is enhanced once the core is in contact with the paper and the crystals are allowed to grow. These crystals are fragile and are easily broken in the mixer or along the belt
    - Once broken, the crystal will not grow and the paper/core bond will not be as strong
- The reverse is also true. If the crystals are already long before the slurry contacts the paper, the interaction will be reduced and the bond will be weaker
    - This can cause blisters and blows to occur

CHEMICAL ADDITIVES –

Accelerators

As the speeds of the board line increase, faster setting times are necessary

Two types of accelerators are used today:

- BMA - landplaster that has been ball milled and blended with additives such as sugar, starch or lignosulfate
- Potash (potassium sulfate) or ammonium sulfate or aluminum sulfate
- These form a complementary effect
  - BMA causes a quick set by forming longer crystals than ground gypsum
  - While the more soluble potash promotes a snappy set as it causes the gypsum crystals to precipitate faster

Retarders

These additives are used to offset the stiffening action of an accelerator and the initial setting in the mixer, due to under calcined stucco

Basically, it retards the set with carboxylic acid groups (-COOH). Retarders will enhance the fluidity of the mix, allowing better mixing of foam into the slurry

Three types are currently in use today:

- Proteinaceous sources, which contain amino acid oligomers or synthetic compounds mimicking the same
- Chelates, such as DTPA and EDTA, provide similar chemical action
- Organic acrylates (i.e., polyacrylic acid compounds)

Boric Acid

- Boric acid raises the calcination temperature for gypsum, thereby protecting the wallboard from the effects of over-drying
- Water soluble, it migrates to the surface of the board, as well as the ends and edges, during the drying process
- It forms a thin layer and modifies the gypsum crystals, making them larger and thicker. This contributes to the rigidity of the boards, thus reducing the sagging tendency
- It increases the density at the interface with the paper. This dense layer is resistant to over-drying. The added layer of protection allows the boards to be processed more rapidly through a hotter dryer, thus speeding up production

Starch

- Acid hydrolyzed starch is used in wallboard manufacturing to allow the use of high temperatures in the kilns, >260^{o}C (>500^{o}F)
- At these higher temperatures, the gypsum crystals can calcine at the paper/core interface, causing that bond to be weak, thus reducing the board strength
- During the drying stage, the solubilized starch migrates to the interface with the water, coating the crystals and preventing them from drying out
- If insufficient starch is present or is not soluble enough, paper peel may develop
- Too much starch can hold water so tightly that more energy is required to remove the water. This increases drying times and energy costs

Others

Sugars

- Dextrose can be used in wallboard as a humectant to control water release and to prevent brittle edges during drying

Water resist

- Silicone & waxes are used for water resistance

Cellulosic fibers

- Cellulose fibers provides exceptional panel and bond strength and low surface absorption

Fibreglass fibers

- Fiberglass fibers to produce a thin, lightweight, yet strong material

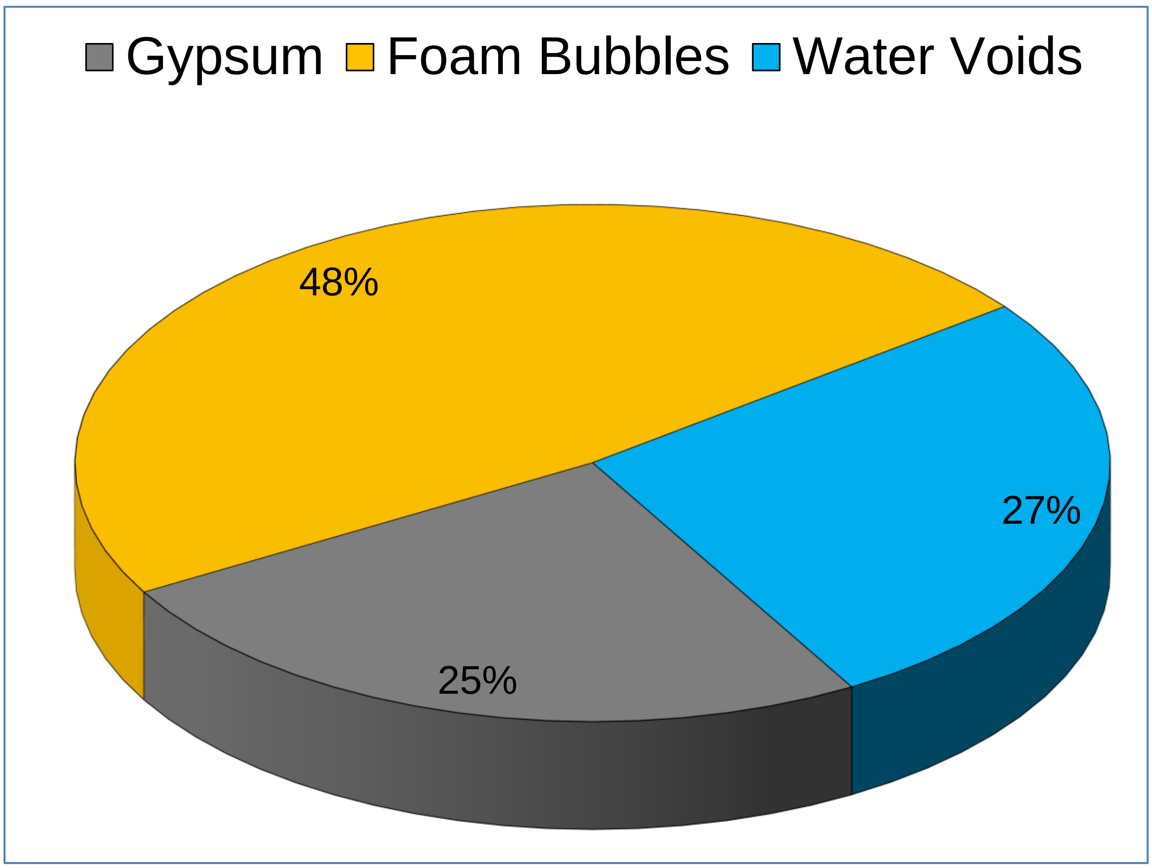
Vermiculite

- Increases fire resistance along with the fiberglass

Gypsum Board Trends

- North American board weight:
    - 1,600 lbs./MSF (7.8 kg/m^2) past;
    - 1,500 lbs./MSF (7.3 kg/m^2) present;
    - 1,200 lbs./MSF (5.9 kg/m^2) new
- At 1,500 lbs./MSF, the board core is mainly **A I R**

Volume in Board (1,500 lbs./MSF or 7.3 kg/m^2)



Foaming Agent

Background

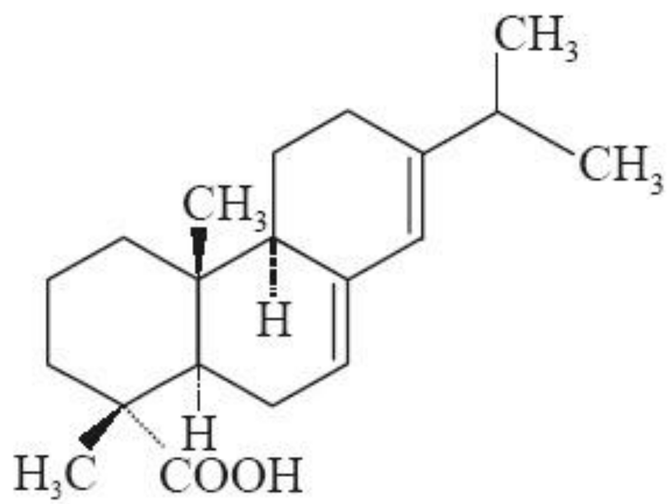
If gypsum wallboard, ½ inch (12.7 mm) thick, could be made solely from stucco, the weight would be ~5,500 lbs./MSF (26.9 kg/m^2)

When this size board is made with stucco and water, the weight would be ~2,700 lbs./MSF (13.2 kg/m^2)

- Water of hydration and excess water are needed to make the gypsum slurry fluid enough to form the board
- Excess water when removed during the drying stage leaves small voids in the core, making the board lighter

To reduce board weight to usable levels and aid installation, more air voids were needed to achieve board weight of ~2,000 lbs./MSF (9.8 kg/m^2)

(I) **The 1st generation** of foaming agent used to further reduce the board weights was achieved with the use of rosin soaps to create air voids in the core. Containing mainly abietic acid, this was a low cost product that produced the desired foam;



Abietic Acid

Rosin soap was replaced by a more efficient soap that had higher solubility in the gypsum slurry, namely, alkyl ether sulfates;

(II) **These 2nd generation** molecules can be custom built with a hydrophobic alcohol end, and a hydrophilic opposite end by adding ethylene oxide and a sulfate group

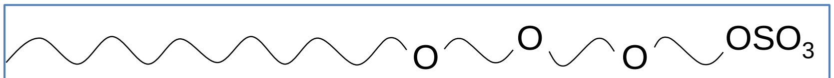
Thus, by varying the alcohol carbon length and the amount of ethylene oxide (EO), a highly effective foaming agent is created;

The hydrophobic alcohol groups are either:

C_8 – C_{10}
C_9 – C_{11}
C_{10} – C_{12}

The hydrophilic group on the alcohol is:

Ethylene oxide (**2 – 3 EO**) sulfate, alkali salts



Alkyl ether sulfate

Air is injected so that the bulk of the core volume is made up of air voids, allowing a reduced weight of ~1,700lbs./MSF (8.3 kg/m^2)

(III) **The 3rd generation**

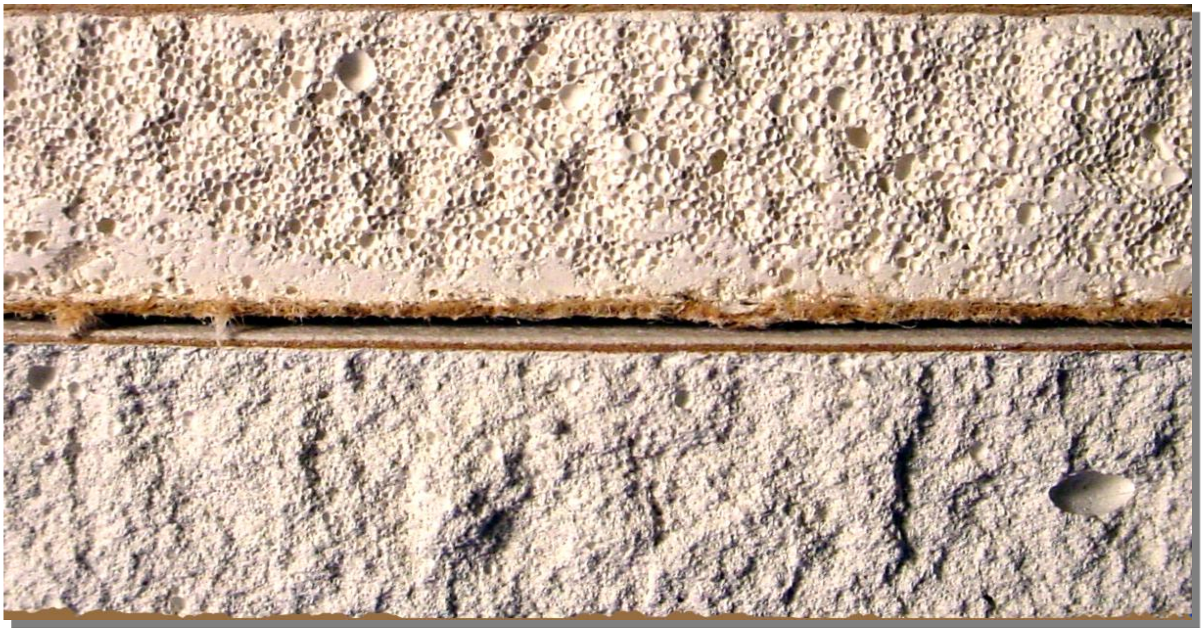
The foaming agents GEO Specialty Chemicals, Inc. invented (Savoly et al., U.S. Pat. Nos. 5,158,612 and 5,714,001). are mixtures of stable and unstable surfactants in specific ratios to produce a mixture of small and bigger foam bubbles in the gypsum core. It has been discovered that foamed gypsum strength is in fact best maintained by incorporating larger size voids in the gypsum.

Improvements have been recently made to the strengthening of the wallboard by producing a properly distributed air void system; via the Hyonic® PFM soap system that achieves higher nail pull strengths. This allows the reduction of board weight to 1,200 lbs./MSF (5.9 kg/m^2), while maintaining ASTM nail pull standard.

Added benefits to this system are:

- Increased evaporation rates due to the close packing of the air cells in the core, thus allowing thin channels and passages around and between the gypsum crystals
- Better wet and humid bonds are also achieved due to the enhanced paper/core bond that is obtained with better wetting ability of the paper's bond liner

Hyonic® PFM system



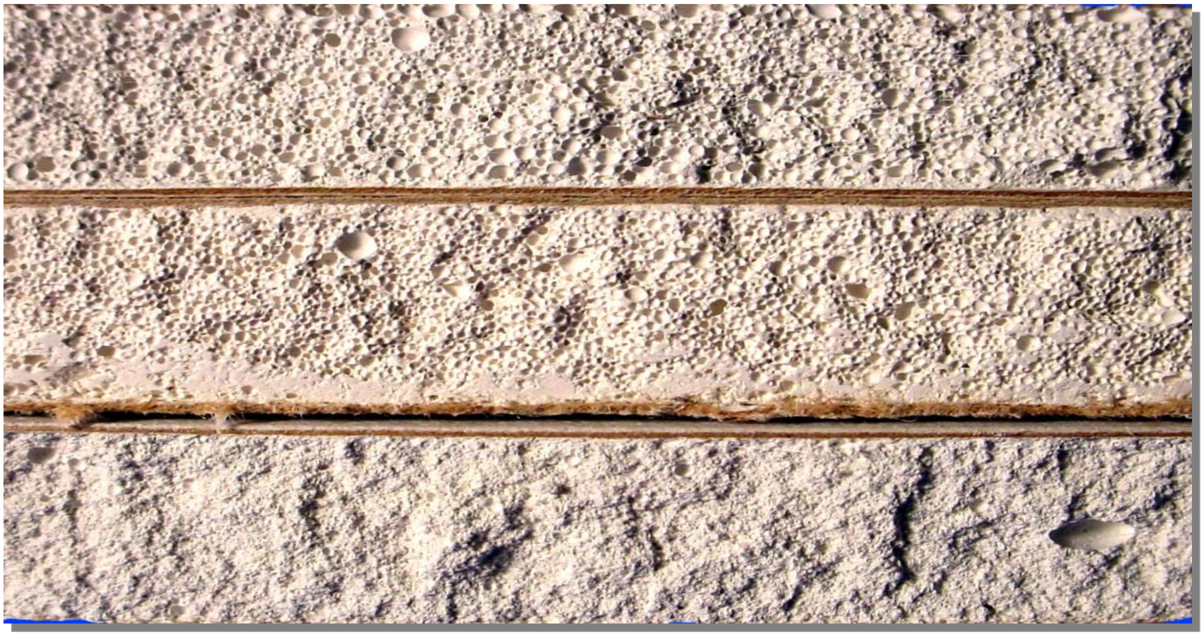
Normal Alkyl Ether Sulfate

By using the Hyonic® PFM soap system, the nail pulls are:

- Increased by +17%, versus regular soap systems and
- Increased by +27% when using the Aero™ Technology (combination of Hyonic® PFM and Diloflo® dispersant)

When the Aero™ system is used, a variety of air voids can be incorporated in the wallboard core to suit nail pull requirements and the market

Dispersant	Dispersant (lbs./MSF)	Foaming Agent	Foamer (solids) (lbs./MSF)	Board Weight (lbs./MSF)	Nail Pull (lbs.)
PNS	**4.00**	**AES**	**0.135**	**1,609**	**75.5**
PNS	**4.00**	**Hvonic®**	**0.135**	**1,634**	**88.0**
Diloflo® CA-30	**4.00**	**Hyonic®**	**0.135**	**1,641**	**96.0**



GEO Specialty Chemicals, Inc. has discovered that when a higher molecular weight dispersant is used, the dispersing effect is increased, and an synergistic interaction occurs between the dispersant and the foaming agent that produces a gypsum wallboard core effect that more efficiently entrains air (i.e., creates void space), U.S. Pat. No. 7,033,432.

This dispersant and foaming agent combination is useful in the production of gypsum wallboard and other aqueous cementitious products. This combination, according to the invention, increases the void size of air that is entrained in the gypsum wallboard increasing the strength of the wallboard (via nail pull), thereby allowing one to reduce the density and overall weight of the final product.

Furthermore, the dispersant and foaming agent combination according to the invention reduces the amount of water required to obtain a free-flowing aqueous core slurry, which reduces the energy costs necessary to cure and dry the gypsum wallboard thereby decreasing production time.

Dispersant

A dispersant can be added to wallboard stucco mixtures to improve workability. In order to reduce the energy in drying wallboard, less water is added, which makes the gypsum mixture very unworkable and difficult to mix, necessitating the use of water reducers or dispersants. Some studies also show that too much of lignosulfonates dispersants could result in a set-retarding effect and data showed that amorphous crystal formations occurred that detracted from the mechanical needle-like crystal interaction in the core, preventing a stronger core. The sugars, chelating agents in lignosulfonates such as Aldonic acids and extractive compounds are mainly responsible for set retardation. These low range water reducing dispersants are commonly manufactured from lignin, a by-product of the paper industry.

High range dispersants have been generally been manufactured from sulfonated naphthalene condensates, although polycarboxylic ethers represent more modern alternatives. Both of these high range water reducers are used at 1/2 to 1/3 of the amount used with lignosulfonates types.

Traditional lignosulfonates and naphthalene sulfonate based dispersants disperse the flocculated gypsum particles through a mechanism of electrostatic repulsion. In normal dispersants, the active substances are adsorbed onto the gypsum particles, giving them a negative charge, which leads to repulsion between particles. The long molecules wrap themselves around the gypsum particles, giving them a highly negative charge so that they repel each other.

A large amount of excess water is generally required to provide the gypsum slurry with sufficient fluidity during the process. It is desirable to reduce the amount of excess water to save energy and production cost associated with water removal.

Water reducing agents are:

- **(I) Lignosulfonates**
- **(II) Naphthalene sulfonate polymers**
- **(III) Acrylic-polyether comb-branched copolymers have also been used as water reducing agents.**
  - The comb-branched copolymers can be used in lower dosages than other sulfonates but tend to retard the setting and adversely affect foam development
- **(IV) 2nd generation Naphthalene sulfonate polymers**

Water in the slurry mix is primarily used to rehydrate the stucco to landplaster.

Second, it is used to wet the paper to produce a good crystal interaction with the paper fibers at the paper/core interface.

Excess water is used to create a fluid stage to allow the flow of stucco to form wallboard. This requires significantly more water than is needed to hydrate the stucco.

The gypsum crystals grow into the needle-like structures which interlock with the paper fibers that are protruding from the bond liner of the paper. This effectively increases the paper/core bonding mechanically.

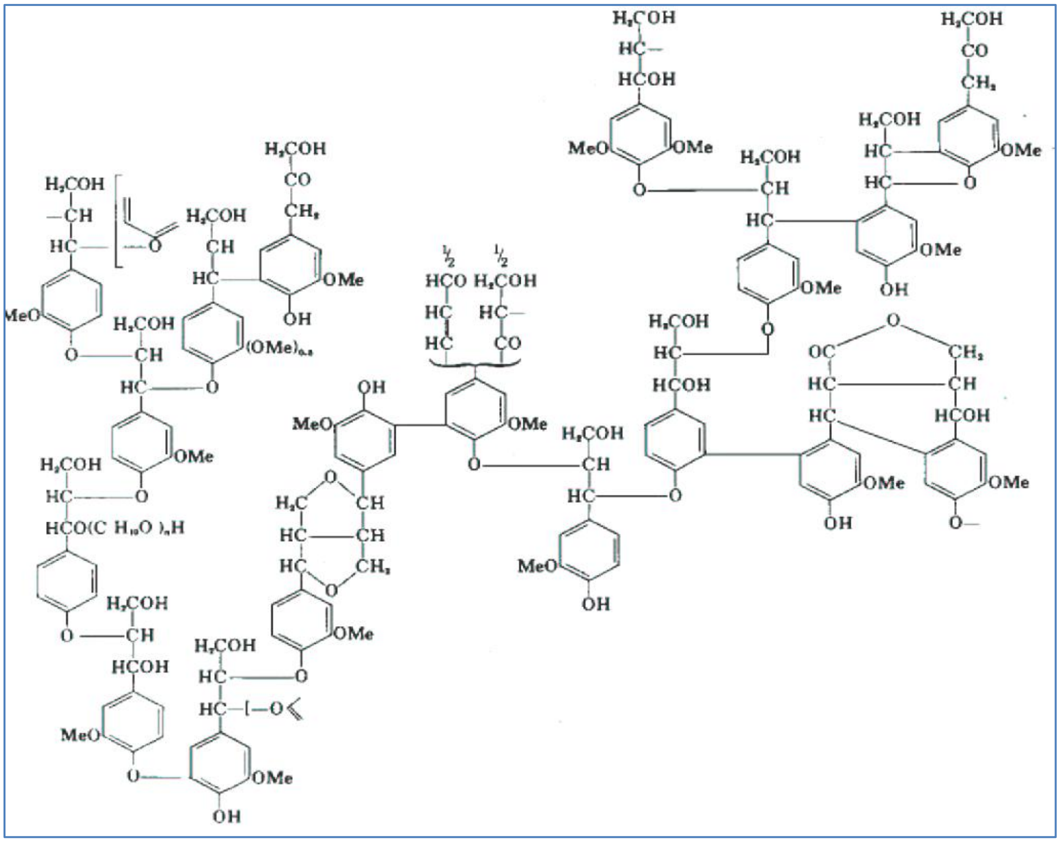
The excess water is removed in a costly drying step.

This was the first inherent reason behind the use of an organic dispersant.

Energy is required to evaporate the excess water from the formed board.

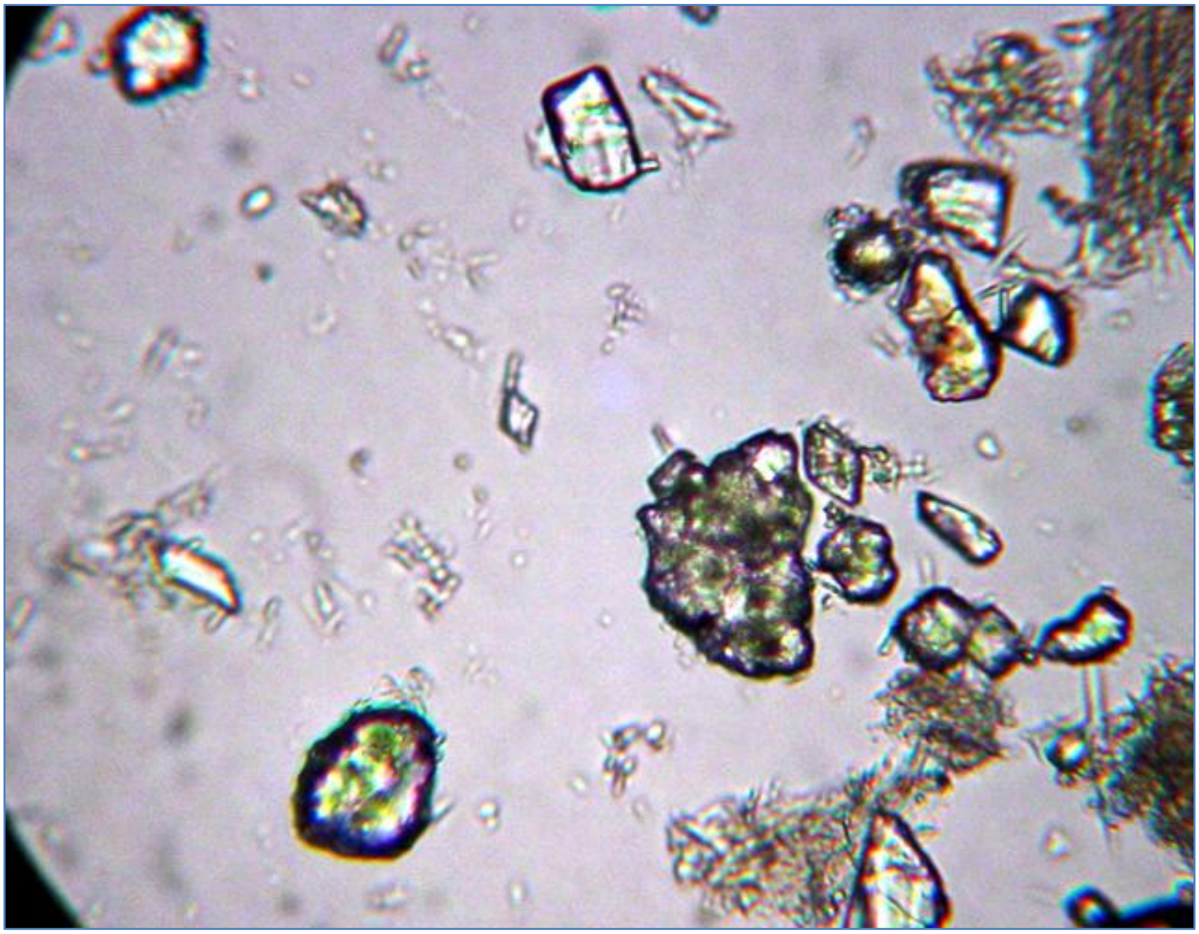
(I) Lignosulfonates

The Lignosulfonates dispersants were a natural, cheap and readily available byproduct:



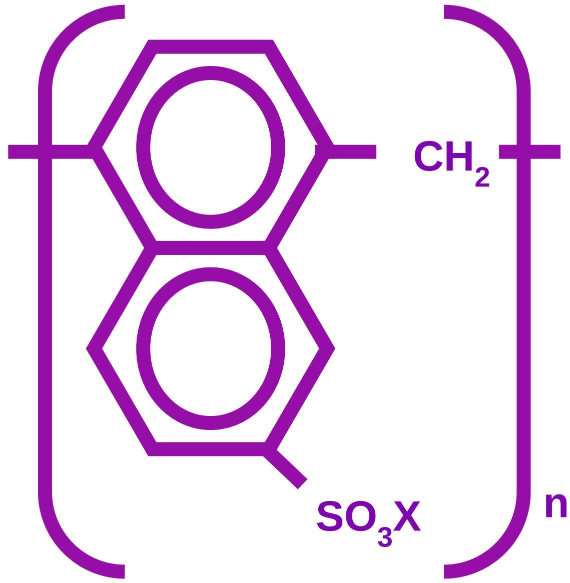
- The Lignosulfonate achieves higher fluidity by coating the stucco crystals and providing an anionic charge to the surface that creates repulsion of like charges
  - Since particles are separated, higher fluidity is achieved by particles not agglomerating
- Water reduction can be achieved to bring the fluidity of the gypsum slurry back to the board forming stage. This water reduction allows the wallboard plants to use less energy in the kilns to dry wallboard
- Or keep kiln temperatures as they were, and increase line speed to increase production
- Typical addition levels for lignosulfonates are of the order of 1 – 3 lbs./MSF (4.9 – 14.7 g/m^2) liquid in ½ inch (12.7 mm) wallboard
- Increasing the dosage of this type of dispersant to achieve higher fluidity and thus greater water reduction, could not be achieved without the detrimental effects of retarding the set and creating secondary foam formation
- This was also detrimental to board formation. Even at lower dosage levels, set retardation occurred and at higher dosages core problems were encountered
- **Microscopic picture below showed** that amorphous crystal formations occurred that detracted from the mechanical needle-like crystal interaction in the core
- Chelating agents in lignosulfonates such as aldonic acids and extractive compounds are mainly responsible for retardation
- **The lower molecular weight fractions also caused performance problems**
- The removal of these problem-causing compounds added much to the cost to this type of product

Lignosulfonates



(II) PNS Dispersant

- The next generation of dispersant used in wallboard production is based on a synthetic polymer, whose properties are controlled and are capable of achieving greater fluidity of the gypsum slurry, without the detrimental side effects of lignosulfonates
- This type of synthetic product is based on Polynaphthalene sulfonates
- Introduced to the U.S. wallboard industry in 1984 by GEO Specialty Chemicals, Inc. (then part of Diamond Shamrock Corp.) as Diloflo® GL

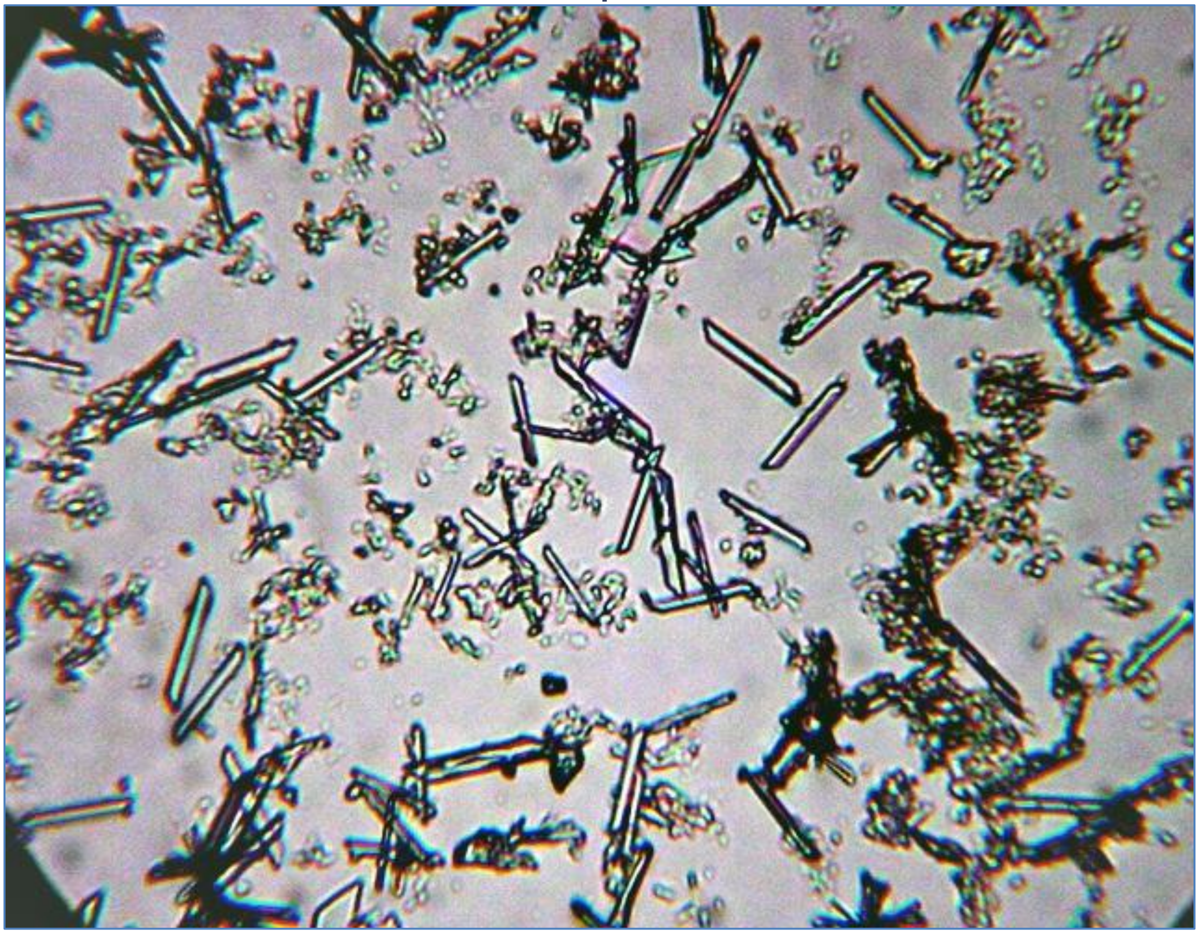


X = Na, Ca, K or NH_4

Benefits:

- Raw materials are at a high purity
- Degree of sulfonation can be controlled to meet a specific criteria
- The polymer content, molecular weight and configuration can be controlled during manufacture
- No set retarding or detrimental low molecular weights are present
- After drying, the frictional forces of these crystals increase the strength of the core. This helps in the handling of the wet board
- With PNS dispersant, the gypsum crystals are closely interwoven (**see picture**), giving the core most of its wet strength

PNS Dispersant



- Addition levels well above 3 lbs./MSF (14.7 g/m^2) liquid, in ½ inch (12.7 mm) wallboard, can thus be achieved to reduce water content of the slurry, without detrimental effects
- With Polynaphthalene sulfonates, only **1/2 to 1/3** of the dispersant amount is needed, compared to lignosulfonates, to obtain equal fluidity
- Microscopic data also shows that when lignin sulfonate is mixed with PNS, detrimental crystals are formed, rather than the favorable needles that occur with just with PNS

The trend in board making in North America has been towards lighter and stronger boards. There are many reasons for this:

- Lower energy cost to evaporate the water
- Ease of handling during installation
- Reduced shipping costs for wallboard, as it is a high weight product with relatively low value
- While the advantages of lightweight boards are many, making a quality lightweight board is not simple
- Lighter weight means less gypsum in the board as a whole, and in particular less gypsum at the paper/core interface and at the edges and ends
- The less gypsum at the interface, the easier it is to over-dry, or calcine, the surface
- When the gypsum crystals at the surface are calcined (converted back into their hemihydrate form), they lose their strength and the bond between the gypsum and the paper can fail
- Obviously this “splitting” is a serious quality issue

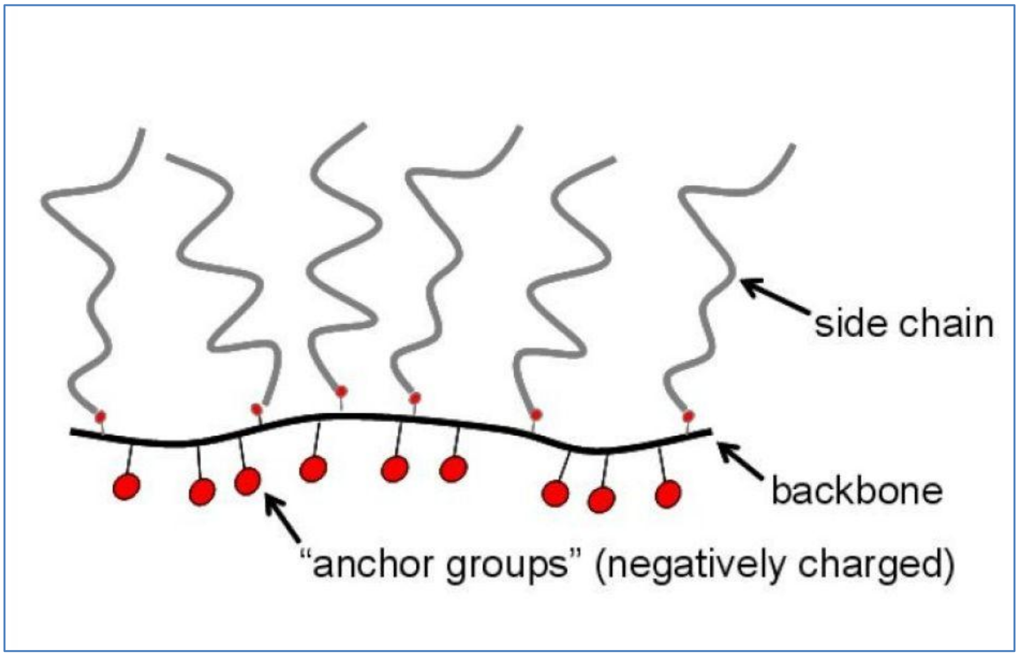
(III) Acrylic-polyether comb-branched copolymers

The next generations of dispersants are polycarboxylate ether-based superplasticizers (PCEs). With a relatively low dosage they allow a water reduction due to their chemical structure which enables good particle dispersion.

PCEs are composed of a methoxy-polyethylene glycol copolymer (side chain) grafted with methacrylic acid copolymer (main chain).

The carboxylate group $–COO^{-}Na^{+}$ dissociates in water, providing a negative charge along the PCE backbone. The polyethylene oxide (PEO or MPEG) group affords a not uniform distribution of electron cloud, which gives a chemical polarity to the side chains. The number and the length of side chains are flexible parameters that are easy to change. When the side chains have a huge amount of EO units, they lower with their high molar mass, the charge density of the polymer, which enables poor performances on particle suspensions. To have both parameters at the same time, long side chain and high charge density, one can keep the number of main-chain-units much higher than the number of side-chain-units.([1])

PCE



Although greater water reduction is achieved with PCEs, there are various egregious properties that were encountered during gypsum wallboard production;

- Gypsum slurry set retardation
- Large unstable, uncontrolled foam bubble size
- The PCEs cost is much greater than the PNS outweighing its benefits

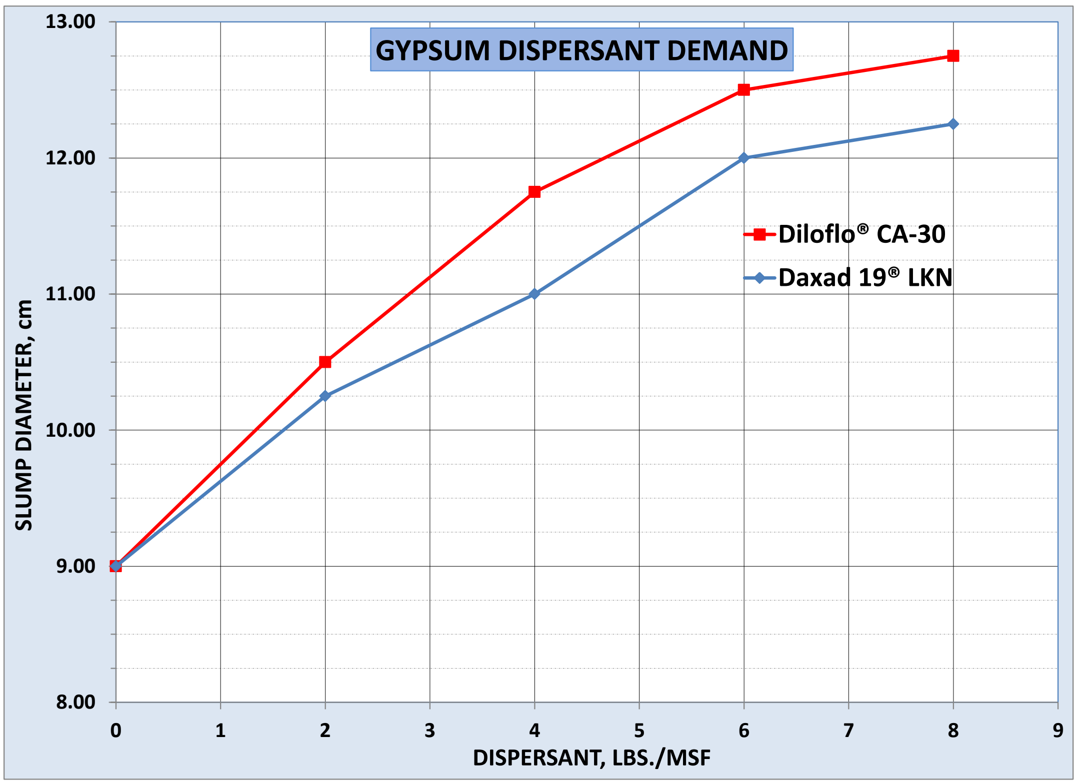
The line board line speed requires gypsum set time in less than 2 minutes and to achieve board strengths, a controlled foam bubble structure is necessary.

([1]) https://en.wikipedia.org/wiki/Superplasticizer

(IV) 2nd Generation PNS Dispersant

The need for increased water reduction and the non-interference of dispersants with the soap was overcome with:

- A new generation of gypsum dispersant that has been introduced, Diloflo® CA-30, based on the polynapthalene sulfonate molecule but tailored to perform better with the Hyonic® PFM series of foaming agents
- The combination of this dispersant and foaming agent enhance the properties previously mentioned, namely:



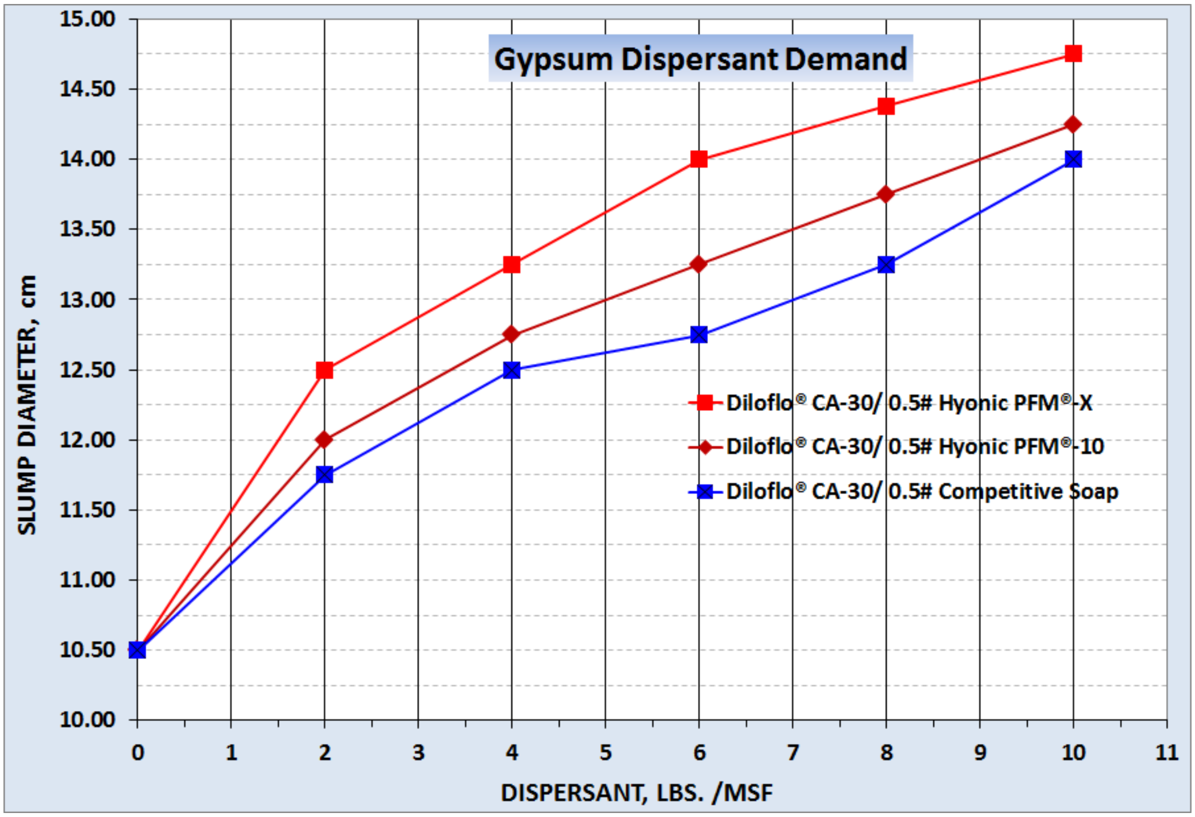
- Higher water reductions than seen normally with regular dispersants and soaps
- Increased wet bond
- Reduced drying times through higher evaporation
- Increased production rates
- Increased nail-pulls that allow reduced board weights
- Lower freight to ship the wallboard

Conventional dispersants used in the production of gypsum wallboard typically have a weight average molecular weight that works well in concrete. At these molecular weights the molecular weight differences have negligible effect on efficiency of the dispersant, and at this molecular weight, there is virtually no detectable interaction between the dispersant and foaming agents. When a novel molecular weight dispersant is used (Diloflo® CA-30), the dispersing effect is increased, and a synergistic interaction occurs between the dispersant and the foaming agent that produces a gypsum wallboard core effect that more efficiently entrains air (i.e., creates void space).

The core of a gypsum wallboard formed using the dispersant and foaming agent combination includes large air bubbles (i.e., large void spaces) with small air bubbles (i.e., small void spaces) dispersed throughout. Despite the substantial increase in the volume of air bubbles or void spaces in the hardened core, gypsum wallboard formed using the dispersant and foaming agent combination according to the invention exhibits a higher nail pull value than gypsum wallboard formed using a conventional dispersant and a foaming agent at the same solids loading ratio.

Diloflo® CA-30 used in the combination is a naphthalene sulfonate-aldehyde condensate alkali salt polymer. The foaming agent is from the Hyonic® PFM series.

The combination of the Diloflo® CA-30 dispersant with the Hyonic® PFM series, i.e. Hyonic® PFM-X, yields a synergistic effect by further reducing the water demand used in the gypsum slurry:



Conclusion

The use of correct chemical additives in the right amount will give you high quality board with the following characteristics:

- Higher water reductions than seen normally with regular dispersants and soaps
- Increased wet bond
- Reduced drying times through higher evaporation
- Lower energy cost
- Increased production rates
- Increased nail-pulls that allow reduced board weights
- Lower freight to ship the wallboard