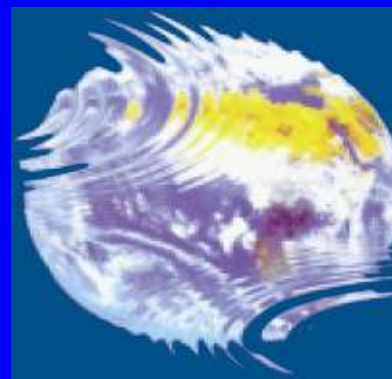


Polyacrylamide Emulsions Handbook



SNF FLOERGER®

General description

■ Standard Emulsions

These are dispersions or suspensions of a hydrogel (hydrated polymer) of water soluble polymer in a hydrocarbon.

They are two-phase heterogeneous systems. The hydrogel is in the shape of microbeads of 1 micron average diameter, it can be considered as a soft solid, their consistency is similar to rubber.

The water proportion varies from 20% to 40% of the final product, depending on the grade. Most of **SNF**'s standard emulsions have a name starting by the two letters **EM**, and some others have a name starting by **EMR** or **FB**.

■ Dewatered Emulsions

Dewatered polyacrylamide emulsions differs from standard by the fact that they contain less than 6% water, with the result that the hydrogel has become almost the dry polymer itself.

The consistency of the polymer is similar to plastic material. Most dewatered polyacrylamide emulsions from **SNF** have names starting by **DW**.

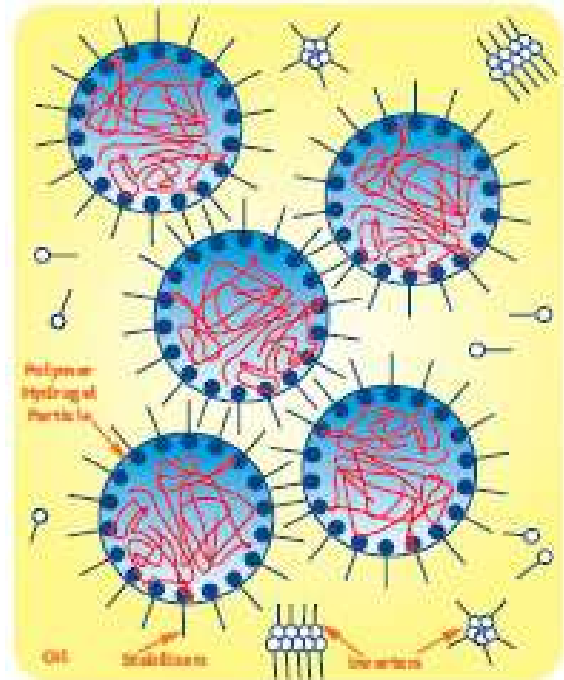
In summary, all emulsions are suspensions of solid particles. Emulsions have a liquid aspect, but they are not pure liquids, nor liquid blends. Nevertheless they can be handled as liquids. But special care must be taken in order to avoid difficulties inherent to the fact that they are not homogeneous isotropic liquids.

Differences between polyacrylamide emulsions and powders

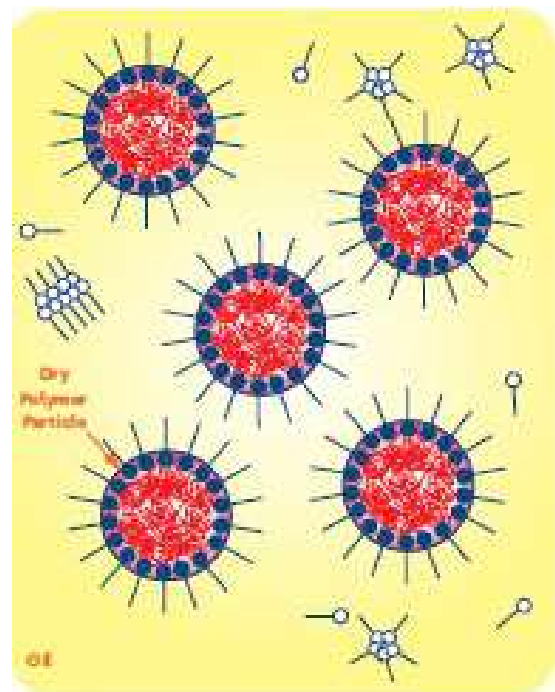
Handling of emulsions using pumps is simpler than powders and in many cases,

in-line injection can be used, avoiding the need for an aging tank. Furthermore, dissolution times are much shorter and there are almost no solubility problems.

Standard Inverse Emulsion



Dewatered Emulsion



Unlike powders, emulsions are complex multicomponent products which include polymer, surfactants, oil and water.

Packaging and transport costs are greater for emulsions. Powders are very stable during storage, whereas emulsions show some instabilities (physical settling, skin formation, etc.). The presence of oil and surfactants involve more regulations for the emulsions than for powders.

In general, emulsions outperform powders on a dry polymer basis and some polymers, with specific chain configurations, can only be prepared in emulsion form.

Emulsions are complex liquids

Polyacrylamide emulsions can be handled as liquid products, but they are not simple liquids. So it is absolutely necessary for users, prior to any operation, to be informed

of the specific recommendations that **SNF** provides hereafter and which concern :

- how to handle them ;
- what care should be taken ;
- what are the problems inherent to the nature of emulsions ;
- how to overcome these problems.



Storage and handling

Storage and handling of emulsions : basic principles

- Emulsions must be stored inside a building at a constant temperature between 5°C and 30°C.
- During the storage and handling, the emulsion must not be contaminated by water.
- Emulsions must not be in a situation where the surface can dry-up by ventilation.
- Emulsions must be sheared as little as possible. Pumping, filtering, stirring, etc. must be applied with maximum care.
- It is highly recommended to follow **SNF**'s recommendations for equipment and conditions for storage and handling.
- In the case of any doubt, it is highly recommended to obtain the advice of a technician from **SNF**.

Notes to readers :

- A common confusion is made by users of emulsions between the commercial form and the final solution of the polymer obtained from this emulsion.

In the following paragraphs we call „emulsion” the commercial product described in page 2 as a polymer suspension in oil. After its dilution in water, this emulsion is destroyed and the result is a true solution of polymer, in which are dispersed droplets of oil which give the solution it's white color.

- Technical details and information on all equipment described in the following paragraphs are found in the **FLOQUIP** brochure available on request from **SNF** or it can be downloaded from the www.snfgroup.com website.

Storage and handling of emulsions : List of situations and operations

Lumps, skins, gels, in the emulsion

■ Normal emulsions

The main causes for the formation of lumps, skins and gels are :

- emulsions are submitted to very cold or freezing temperatures ;
- emulsions undergo cycles of warm and cold temperatures ;
- too much shear is applied ;
- water contamination ;
- pollution by foreign matter or by dried polymer.

■ Effect of very cold or freezing temperatures

Most often this happens when an emulsion is stored outside and when the container is not closed. Emulsion has a tendency to dry-up especially when it is a thin layer. This happens on surfaces or walls which have been temporarily wetted by the emulsion. The upper surface of the product in the container (drum, pail, etc.) will behave the same way, especially if the container is open to air.

As polyacrylamide is very easily film-forming, when this layer is submitted to freezing it become a skin. Polyacrylamides are film forming, so when a layer is subject to freezing temperatures, a solid gel like skin is quickly formed. This skin can finally be removed from the surface, fall in the product and contaminate the emulsion with soft solid large lumps which cannot be re-homogenized.

■ Effect of cycles of warm and cold temperatures

The observations are called raincycle. A typical example of raincycle is described below :

„A container of emulsion initially at a temperature of 20°C in a warehouse, is placed, for several hours outside where the temperature is 5°C. The water vapour contained in the free volume above the product condenses and drops of water formed on the roof of the container fall down on the surface of the emulsion, creating local coagulations.”

Gel formed looks like white stringy lumps floating on the surface or suspended to the cover of the drum or container.

■ Water contamination

There are also problems in the case of water contamination or if the components of the pump have not been dried properly after washing with water, or with the involuntary backwash of dissolution water during shut off of the system.

Design of the make-up system is critical and must be made in such a way that there is no possibility of water back-flow from the main water supply into the emulsion piping. Also any other contact between water and emulsion (like rain for example) will generate white stringy lumps.

Too much shear applied when handling pollution by foreign matters or dried polymer.



After the shelf life of an emulsion has been exceeded, free flow gravity filtration from container to container is recommended to recover the emulsion.

■ **Dewatered emulsions**

For dewatered emulsions, the situation is different. They are not concerned by raincycle. As the content of water is very low, there is no formation of skins and lumps during freezing or when they are submitted to cycles of warm and cold temperatures.

Therefore, the only caution to be followed is that dewatered emulsions must be stored at temperatures above 5°C. Below 5°C they become very thick and below 0°C they do not flow and have a consistency of butter.

■ **Important information**

Therefore, even if the final user has appropriate storage facilities and follow strictly all **SNF**'s recommendations, problems can still occur during transport

or during intermediate storages.

SNF invites its customers to be prepared to have to restore the product as it is described here.

■ How to restore the product

In such a situation, **SNF** recommends to transfer by gravity, without previous agitation, in a free-flow mode to another container, while passing through a large area bag filter having a mesh size of 750 microns and above (See “*Filtering an*

Settling”

■ Main observations

After some time in storage, a layer of oil (translucent, amber) appears at the top of the product and a thickened layer of emulsion appears at the bottom.

The reason for this is that the internal dispersed phase (the hydrogel of polymer) has a higher density than the continuous oil phase, so they have a natural tendency to separate.

Emulsions start to settle as soon as they are left without agitation. It is a normal behavior.

It is very difficult to predict how fast and how much an emulsion will settle. It depends on the grade, the batch, the temperature of storage and many other parameters. In most cases, the oil phase layer cannot be observed before 3-4 months. For dewatered emulsions, no settling can be observed during the first 12 months.

■ How to avoid problems

Emulsions which are going to be stored for long periods (more than 1 month) should be homogenized before use. Homogenization must be made by gentle agitation and short periods.

■ Recommendations concerning agitation

emulsion”, page 6-7).

For customers supplied in standard 1 tonne containers (tote-bin, IBC), **SNF** recommends specifically designed equipment called the **Floquip SE** for this operation.

For bulk deliveries, filtration at reception is recommended between the truck and the storage tank.

Too strong or too long agitation can provide too much shear to the emulsions and destabilize them. Agitation by recirculation is not recommended, but in case where there is no other way, avoid the use of pumps giving a strong shear and any device creating an increase in pressure drop in front of the pump (ex : check valves).

Agitation by sparging with air (only dried air) is also possible but less recommended.



Filtering an emulsion

■ Generalities

Emulsions are filtered at 300 microns, after production and before packaging. Filtering an emulsion is an operation which apply shear on it, and shear can destabilise the emulsion. So, it is recommended to avoid as much as possible to do filtrations and proceed only when necessary.

■ When to filter

When the presence of lumps, gels, skins, etc. is observed in the emulsion. See paragraph “*Lumps, skins, gel, etc. in the emulsion*” page 4).

Manual Filtering



■ How to filter

■ Other recommendations

Avoid filtration at mesh size below 750 microns.

Avoid use of small diameter piping.

In line filtration just before use is not recommended.

Do not agitate the emulsion before filtration.

Color of the emulsions

Most of the emulsions are opaque, some are slightly translucent. The most general shade is off-white, some are creamy yellowish, some greenish and dewatered emulsions (DW) are milky white.

As emulsions are multiphase systems and are composed of sometimes more than 10 components, slight color changes which are impossible to control may occur. Variations can come from stabilizers, residues of the

SNF recommends to filter through a bag with a large area. The recommended mesh sizes are 750-1000 microns.

The best process is to transfer the emulsion to be filtered by gravity in a free-flow mode to another similar empty container. For filtration of large quantities (e.g. transfer from tank-truck to a storage tank) in-line filtration can be made using a house filter equipped with the same kind of bags.

Typical filter bags for filtering an emulsion



catalytic system, surfactants and oil which are never totally pure products, slight differences of raw material between suppliers, etc.

Furthermore, slight differences in statistical distribution of molecular weight of the polymer and size of the beads of polymer may generate changes in the refractive index of the components and lead to slight color variations.

Color changes can also occur during the storage (due to temperature differences,

UV light, etc.), and some pails may behave differently within the same batch, quite at random.

It is absolutely impossible to predict or control such limited color changes. This parameter is not considered as a quality issue. Performance studies versus color changes have been made on different applications. They have concluded that color fluctuations have no impact on the performance.

Pumping an emulsion

Among the difficulties of pumping an emulsion are those generated by the following actions occurring during the handling of the emulsions :

- shearing
- pinching or gripping
- rubbing

Such actions happening repeatedly lead to the destabilization of the emulsion. Polymer particles agglomerate, form lumps that stick on equipment. This mostly take place in the pumps.

The importance of these difficulties depends on the pumping conditions. Two critical parameters must be considered: pressure drop and cleanliness.

Pressure drop

The pressure drop at the discharge of the pump is created by :

- important pipe length ;
- small pipe diameter ;
- elbows on the lines ;
- equipment on the lines (especially mass flow meter) ;
- hydrostatic pressure ;
- valves and check valves.

The higher the pressure drop at the discharge of the pump, the more shearing gripping and rubbing will take place in the pump.



Cleanliness

It is well known that emulsions left on a surface in open air conditions will dry up. After a few hours appears a film/skin that sticks to the surface. When this happens in an equipment which is used regularly but discontinuously and is never cleaned, several skins/films can be deposited always at the same place and a thick crusty layer develops.

After a while, this layer will finally detach from where it has been formed and contaminate the product.

Finally these particles may arrive in the pump and if they do not plug or block it immediately, they will nevertheless affect its running in a way which will generate shearing gripping and rubbing.

Result of a bad maintenance and of an inappropriate installation.



Pumping experience

End-users use metering-pumps to feed the emulsion in the water through various make-up systems to prepare the polymer solutions. Every end-user of polyacrylamide emulsions has its own specific operating conditions and equipment. In order to anticipate pumping difficulties it is necessary to know the behaviour of all kind of pumps under various conditions. **SNF** has a long experience on this subject.

There are many kinds of metering pumps. Some have been tested in the past and have been given up because of very bad behaviour when used with any type of emulsions.

These are, for example, gear pumps, lobular pumps, pallets pumps and all pumps providing too much shearing, pinching, gripping and rubbing.

The more sensitive part is the mechanical seal.

Lower friction will limit fouling



Peristaltic pump



SNF has extensive experience on three kinds of metering pumps that work with emulsions

- † Piston/membrane pumps
- † Progressive cavity pumps
- † Peristaltic pumps

Standards emulsions

When pumping standard polyacrylamide emulsions (EM, EMR, FB) all three kinds of pumps can be used.

SNF recommends the progressive cavity pumps for all normal and usual cases.

In case of high pressure drop at the discharge of the pump or if there is a presence of polymer particles as described above, a peristaltic pump is recommended. When piston/membrane pumps or progressive cavity pumps are used, pinching, gripping and rubbing of the emulsion is increased and plugging after a long period of use can happen.

When there is a high pressure drop at the discharge of the pump, **SNF** recommends

using peristaltic pumps for standard emulsions.

Dewatered emulsions

Piston/membrane pumps and progressive cavity pumps are often used.

Spills

Spills problems may occur. Oil absorbing powders, sawdust, paper can be used to absorb the spills of emulsion on floor. It is important to remove quickly the resulting thick mass, because it turns quickly to a hard crust stinking to the floor, which is very difficult to remove even with high pressure water. In case of spills, **SNF** recommends also :

- for small spills (i.e. few liters) : wipe the spill with large paper towels as well as possible, and then use high pressure water to clean the ground ;
- for important spills : wipe the product in a corner with hand-scrapers and make a dam with planks and sand around to maintain the emulsion and then pump it. After pumping, put sawdust or absorbers or directly wipe the ground with towels. Then use high pressure water to clean.

In any case, avoid absolutely to add water directly on the spill, because the amount of water necessary for a good dilution is very high.

Cleaning

On the surface of any equipment which has been in contact with an emulsion, a thin film remains which will dry (solvent and water will evaporate) and become a skin of

SNF does not recommend this. In cases of high pressure drop at the discharge of the pump or presence of particles of polymer as described above, pinching, gripping and rubbing is increased and on dewatered emulsion generate hard particles which can block very quickly the pump and even destroy it. When pumping dewatered polyacrylamide emulsions (DW), peristaltic pumps are highly recommended by **SNF**.

polymer. In general, it is highly recommended to let this film/skin remain as such, or just simply rinse. Before any rinse it is advised to drain the emulsion as much as possible and then rinse with solvents (kerosine, mineral spirits).

■ **Full cleaning**

For the full cleaning of a tank, the recommended procedure is as follows : Remove as thoroughly as possible the remaining emulsion (dry or wet) on the different parts of the tank, by rinsing with solvent (same as above) or, when there are large deposits which cannot be removed by a simple rinse, it is necessary to wipe manually.

Then fill the tank with hot water and add 2% of caustic. Let the polymer swell and degrade as long as necessary (sometimes it may take more than one day). Then rinse with water or preferably use high pressure water to finish the cleaning.

After any cleaning using water, all the equipment, storage tank, pipe, pumps need to be dried before any contact with emulsion. For this reason, a simple rinse with solvent is recommended.

Cleaning of items of equipment (pumps, valves, fittings, filter cartridges, etc.), which have contained emulsions, follow the same rules as the tanks.

As described above, the complete washing of storage tanks takes time and requires

operations which are not easy. This can be done once a year or, preferably, once every three years, depending on the circumstances, or when it is absolutely necessary for specific reasons. Complete washing must be scheduled in advance and takes at least two days.

All contaminated cleaning solvents and solids must be incinerated.

Contaminated water must be treated by normal methods.



Exposure to high and very low temperatures

Emulsions which have been submitted to prolonged periods of storage at temperatures far beyond those recommended (5°C-30°C) can still be used after restoration. Nevertheless, the loss of product during the restoration is usually quite large.

Storage

Emulsion must be stored inside a building at a constant temperature between 5°C and 30°C.

Small packages recommended by **SNF** are plastic pails (polyethylene), full opening plastic drums, one tonne containers (totebins, IBC). These packages must be closed tightly in order to avoid drying and exchange between outside and inside.

They also must be filled completely to have the minimum void space above the product. After a first opening and partial consumption the package must be closed tightly and complete consumption must take place rapidly.

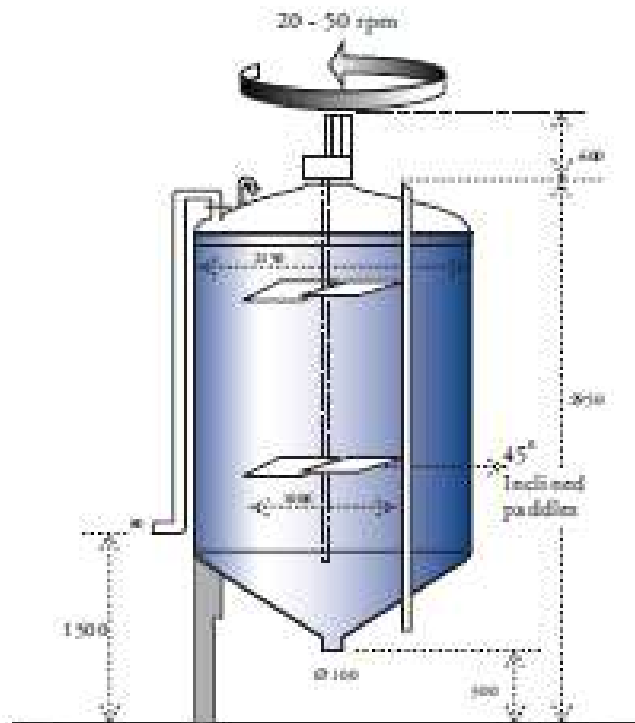
(Because of the increasing void space above the product, the surface of the emulsion can start drying, coagulate and create a skin).

The tank has to be vertical with a conical bottom to help unloading ; it should also be fitted with an inspection manhole to facilitate cleaning.

For anionic emulsions, stainless steel, Polyester Fiber Glass (FRP) or crosslinked polyethylene are suitable. For cationics, FRP tanks or polyester glass coated steel tanks are preferable to avoid formation of rust at the interface between air and the product, which may occur with a stainless steel tank.

Insulation and external electric heating are necessary for outside tanks.

■ Storage tank



Agitation

During storage, emulsion can settle. There are many situations where the motionless surface of the product can dry-up, for example when the product is left in its original packaging partially empty, or left opened, or opened frequently.

It is necessary to homogenize regularly an emulsion by agitation, especially when the time of storage of a tank is higher than 10 days.

Homogenization must be made by gentle agitation for short periods.

An agitation either too strong or too prolonged may apply too much shear to an emulsion and destabilize it.

Typical examples of how to proceed :

- Pails can be shaken 4-5 times by hand before use.
- Drums are not well adapted for long time storage, because it is not convenient to provide agitation to them.

For full opening drums it is possible to adapt a stirrer. But the preferred way is to transfer to an adapted storage tank of 300-400 liters equipped with a stirrer.

The stirring time recommended is 30 min a week or 10 min every 2-3 days and just before use.

- For containers (tote bins) it is possible to adapt a stirrer to the hole, but the best is to use the **FLOQUIP SE** system.

Stirring time recommended : 10 min every 2-3 days and just before use.

- Storage tanks must be equipped with a stirrer with large blades rotating at low speed (ex : 20 rpm with 1 meter diameter blades for 30 tonnes). Stirring time recommended : 30 min 2 times a week or 10 min every 2 days.

Compatibility of emulsions with materials

Emulsions contain or provide at the same time :

- a solvent which reacts with certain plastics and rubbers ;
- a polymer which reacts with certain metals ;

- a pH which varies with the type of product, neutral for anionics, acidic for cationics ;
- and in certain cases, chloride ions which enhance corrosion.

Polyethylene tubing



of emulsions, but the oil has tendency to migrate in low density polyethylene decreasing the drum strength. Treated polyethylene (fluorinated microfibers) are sometimes used with very good results.

The type of equipment and the materials used for the storage and handling of emulsions are very critical due to the very high quality required by many applications.

Polyethylene is used for the transport

The general compatibilities are shown in the following tables :

PLASTICS

Plastic	ANIONICS	CATIONICS
Plasticised PVC (hoses)	very poor	very poor
Polyethylene high density	medium	medium
Polyethylene low density	poor	poor
Crosslinked polyethylene	good	good
Fluorised polyethylene	good	good
Polypropylene	medium	medium
PTFE	very good	very good
PVDF	very good	very good
Fiberglass (FRP)	good	good
Polycarbonate	good	good
Polyamide (nylon)	good	good
Plexiglass	medium	medium
ABS	medium	medium

METALS

	ANIONICS	CATIONICS
Carbon steel	very poor	very poor
Galvanised iron	very poor	very poor
Stainless steel 304	very good	medium
Stainless steel 316	very good (some rust)	medium
Hastelloy	very good	good
Steel coated with polyester and glass flakes	very good	very good
Aluminium	poor	very poor
Copper	poor	very poor
Zinc	very poor	very poor

RUBBERS

In the emulsions the solvent is the component which can affect the stability of rubbers. The following table shows the behaviour of different rubbers after immersion in the solvent during 4 weeks

	Abbrev.	% increase of weight less than 0.1
Viton (fluoro-elastomer of vinylidienne)	FPM	less than 0.1
Perbunan (nitrile/rubber butadiene-acrylonitrile)	NBR	0.1
Hypalon (chlorosulfonated polyethylene)	CSM	0.3
Aflas 150 (tetrafluoroethylene-propylene)	TFE/P	0.4
Perbunan (food grade)	NBRL	1.2
Therban (hydrogenated Perbunan)	HNBR	2
Hypalon low density	CSMh	8
Perbunan low density	NBRh	11
Silicon	Si	58
Ethylene propylene diene low density	EPDMh	61
Silicon low density	SiH	more than 80
Ethylene propylene diene	EPDM	more than 80

This leads to the conclusion that only Viton (FPM) and Perbunan (NBR) are suitable for contact with the emulsions. Jerricans, drums and containers in polyethylene are often used for transport.

If they are non-fluorinated, it is necessary to use high density, thick-walled equipment in order to reduce softening due to the plasticizing effect.

Blends of emulsions

Sometimes situations arise when it may be necessary to blend different emulsions. Most often this happens when there is a product change at a customer site. Maximum care must be taken with blends of different emulsions.

Most of **SNF**'s emulsions are compatible with each other, but so many different blends are possible that it is highly recommended to check and get advice from **SNF** before proceeding.

Two difficult cases :

- Blends between an emulsion from **SNF** and an emulsion from a competitor are to be avoided. Some components (particularly surfactants and oil) are different and can be incompatible.

If there is no other way, it is absolutely necessary to make compatibility tests.

- When a tank has been emptied but not washed and a small amount of the former product remains in the tank, loading the new product on top may very often lead to problems, especially when the tank has no agitator.

Generally, what remains is thickened product. So it is better to completely clean the tank and then load the new product.

Dehydrated emulsions

SNF provides dehydrated emulsions (many of them have the prefix DW, eg DW 533, which is the dehydrated equivalent of EM 533). These products are obtained from normal emulsion after removal of the water content. This results in a more concentrated polymer content.

These products can be considered to be dispersions of polymer in oil. The advantage of this form is the improved stability compared to the normal emulsions.

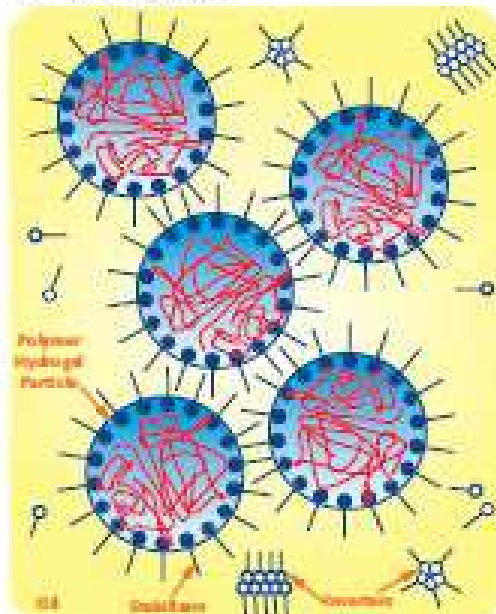
This improvement in stability affects :

- the settlement which is negligible over a period of more than one year ;
- no lumps or skin formations when the product is stored in cold conditions, or submitted to cycles of warm and cold temperatures, or left in conditions where the surface of the product can dry.



Making the polymer solution

Inverse Emulsion



Fundamentals

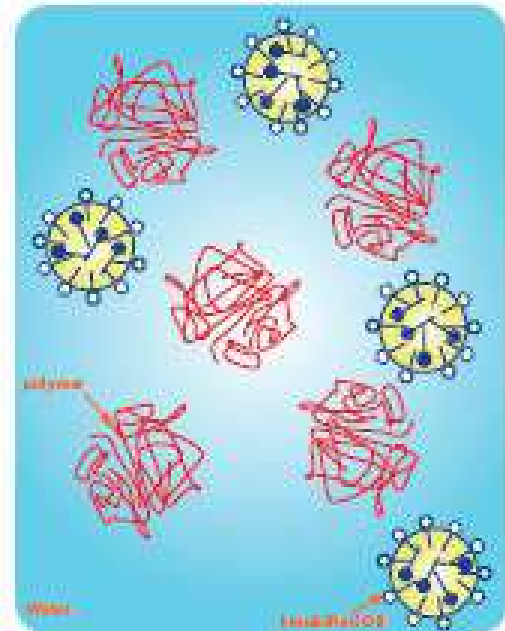
Polyacrylamide emulsions are not simple concentrated solutions of polymer, so a simple dilution in water is not possible. When preparing a polymer solution from an emulsion, there are two physical phenomena (phase inversion and dissolution) which take place and need some specific conditions to be made properly.

When the emulsion comes in contact with water, the inverting surfactant dissolves and emulsifies the oil in the water (inversion). The beads of hydrogel come in contact with water and dissolve (dissolution).

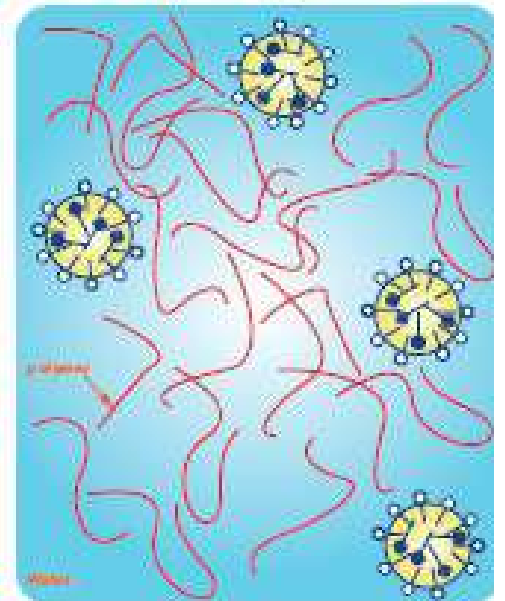
The total time and the quality of inversion /dissolution are dependent on the following fundamental rules :

- Emulsion must be added to the water and not the contrary.
- Very high shear must take place at the point of contact between water and emulsion. Agitation disperses the emulsion in the shape of unitary beads or agglomerates.
- High ratios of emulsion versus water are preferred (the higher the concentration, the higher the speed of dissolution).
- The water must be as soft as possible and not alkaline buffered.
- Temperature of the water must be below 30°C.

Inverted Emulsion



Dissolved Polymer



Details on the main parameters

■ Water quality

Hardness of the water increases the time of aging and may make the solubilisation of the polymer incomplete or impossible.

Calcium and magnesium ions (mainly) reduce the efficiency of the surfactant. With alkaline buffered waters, the same disturbances in the efficiency of the

inversion can be observed and the stability of the final solution is strongly affected. (See paragraph „*Stability of the polymer solutions*” below.)

In hard water (above 300-400 ppm of CaCO_3 or equivalent), the speed of inversion is reduced. For very hard water such as sea water and brines, it is necessary to adapt the formulation of the emulsion to make the inversion possible.

In such a case, the product must be designed specifically and a study should be made separately by **SNF**.

■ **Concentration for inversion of emulsions in water**

To obtain a good inversion of the emulsion, it is necessary for the surfactant to be present at its minimum effective concentration.

Ratios of 5g/liter of active polymer (10-15g/l commercial emulsion) in water are the most efficient.

At lower ratios, the time for aging will be higher or the solubilisation not complete. At higher ratios, the final solution may be too viscous.

In cases of hard water, the ratio must be 5 g/liter of active polymer (10-15g/l commercial emulsion) in water and not below, to give a good inversion.

■ **Shear during inversion**

To obtain a good inversion, it is necessary for each polymer particle to be dispersed separately in water, otherwise the particles will agglomerate.

To ensure efficient dispersion, it is necessary to use high shear mixing at the point of emulsion-water contact.

■ **Make-up systems**

Many types of equipment are available on the market, made by several manufacturers. Some are more or less efficient depending on the characteristics of the application.

SNF provides advice and help in any case based on the above recommendations. In general, any equipment which does not provide enough shear after the contact between emulsion and water will, in many cases, not be efficient.

SNF recommends **Floquip DE** type equipment for emulsion dissolution.

Stability of the polymer solutions

Polymer in water solutions can be unstable and degradation can result in lower efficiency. Each case (based on the emulsion grade used, the kind of water used, the equipment make-up unit, times for aging of the solutions etc.) is different and must be studied specifically.

Hydrolysis

The main reason for instability of the water polymer solution obtained from cationic emulsions is the hydrolysis of the ester

function of the cationic pendant group. Hydrolysis means that part of the cationic groups are transformed into anionic acrylate groups, giving an amphoteric polymer, thus reducing the cationicity. Hydrolysis can occur especially if the water used to make the polymer solution is alkaline buffered water.

Under such circumstances the time for using the solution can be very short and reach in some cases less than 10 min. The solution becomes very thin, full of white fine precipitates and very foamy (sometimes cream may appear at the top of the solution).

The speed of hydrolysis depends on many factors: dilution, water hardness, buffering effect, type of polymer, temperature, etc. Several cationic polymers hydrolyze and especially those made from ADAM-Methyl chloride, which correspond to most of the polymers produced by **SNF**.

The cationicity not only decreases proportionally to the degree of hydrolysis but very often, depending on the pH and salinity of the water, it may decrease at twice this speed due to the interaction between the anionic groups formed through hydrolysis and the unhydrolyzed cationic groups. This is known as the Zwitterion effect.

Anionic emulsions

Anionic emulsions have good stability in the range of :

Anionic emulsions		
Active Content	1 g/liter	5 g/liter
Stability	8 hours	8 days

Cationics emulsions

Water polymer solutions obtained from cationics emulsions are much less stable than those from anionics emulsions.

Cationics emulsions				
Alkalinity	Low	High	Low	High
Active Content	1 g/liter	1 g/liter	5 g/liter	5 g/liter
Stability	1 hour	10 minutes	8 hours	30 minutes
Acid Stabilised Emulsion	4 hours	1 hour	2 days	8 hours

Assessing and limiting hydrolysis

In situations of short term continuous use of solution made with rather soft water, there is in general no need for a special treatment, such as, for instance, the addition of an acid.

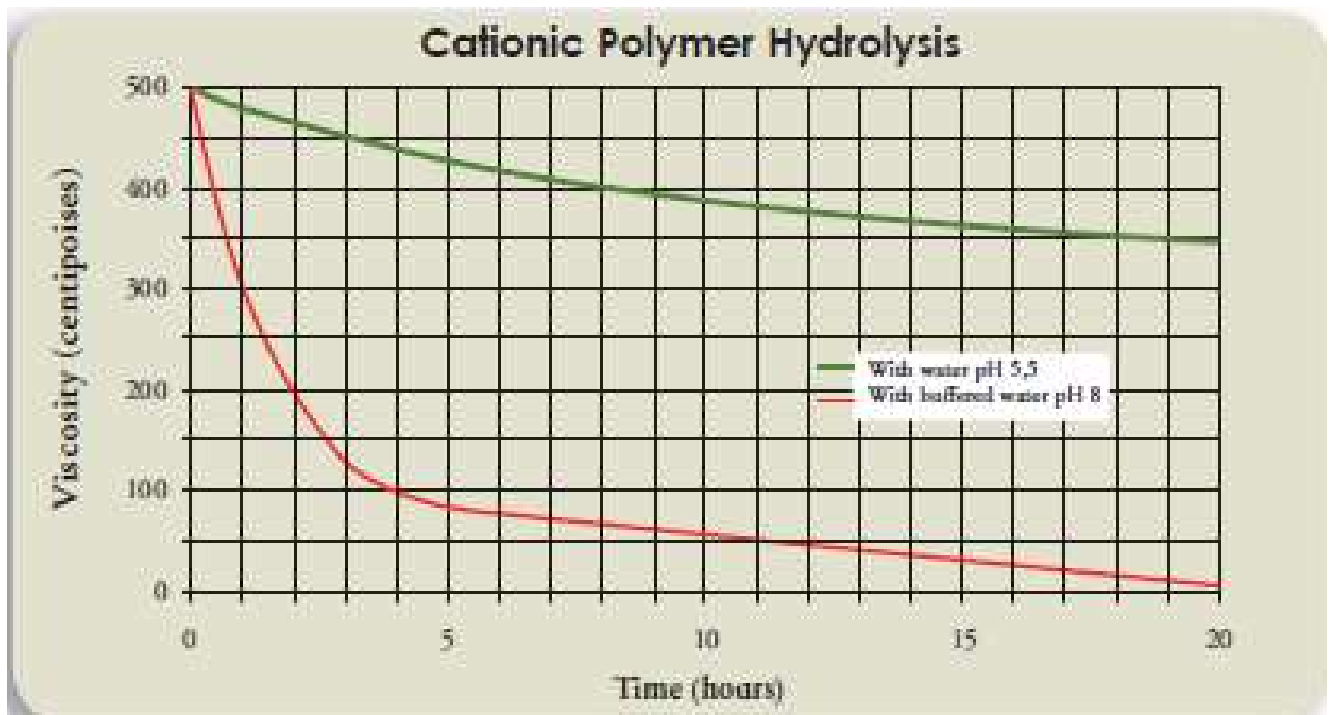
For specific cases, acid addition to the emulsion during production or directly in the solution can be made for stabilisation .

The best pH for stability of solutions at 5g/l of emulsion is below 6.0, and most preferred 5.5. The pH must be measured in the water which will be used industrially.

When the pH is below 6.0, normally the hydrolysis is slow, therefore it can be important to check if there will not be a risk of hydrolysis, in particular when the solutions are prepared a long time in advance.

If the pH is above 6.0 (this is often the case when underground source water is used in papermills, refineries, etc.), or when the solutions are prepared a long time in advance, one or more of the following actions should be taken :

- try to use soft water for dissolution ;
- add buffering acid to the solution to decrease the pH ;
- increase the concentration during dissolution to maintain the pH under 6.0, then dilute continuously just before use ;
- request a polymer from the production plant containing a higher buffering acid content ;
- increase the cationicity of the polymer to be used.



Free radical chain degradation

Polyacrylamides in solution are sensitive to free-radical chain degradation. Free radicals are formed in water by a number of oxidising and reducing agents. Mostly, they are formed from dissolved oxygen and iron. Degradation occurs after about 2 hours at iron concentrations of 0.5 ppm.

Some well waters contain more than 5 ppm iron. In such cases, degradation is high even during dissolution. Iron sensitivity is very difficult to overcome. Chelating agents, for instance, increase the degradation when they are mixed in with the solution.

Treatment has to be on a case by case

basis using the following guidelines :

- since only Fe^{2+} causes chain degradation, aerating the water oxidises it to Fe^{3+} and so reduces the effect ;
- adding a chelating agent before aeration (whenever possible) increases the speed of the oxidation of Fe^{2+} ;
- use of an oxidizer such as perborate at 2 to 4% (based on the active polymer) will rapidly oxidize the Fe^{2+} to Fe^{3+} ;
- increasing the dissolution concentration decreases the Fe^{2+} / polymer balance. This is the easiest solution for Fe^{2+} level in the region of 1 to 2 ppm ;
- use treated water (to be tested) instead of well water. This water is more aerated and normally more

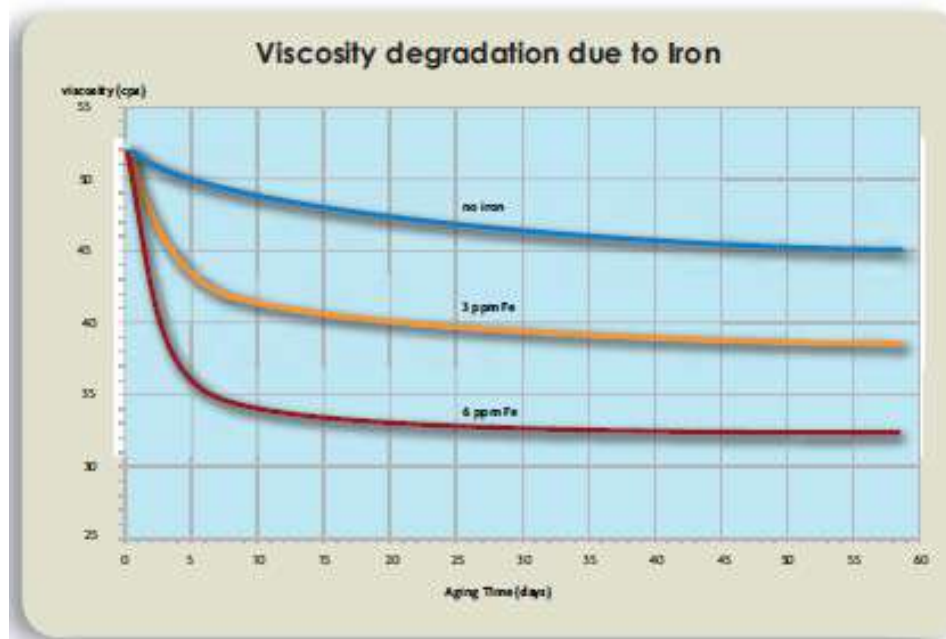
suitable when the clarification is good ;

- use potable water instead of well water but this can considerably increase the cost of treatment.

Based on European statistics, problems due to hydrolysis and free radical degradation are encountered with 30% of all cationic polymers, especially in municipal water treatment plants and paper mills.

Emulsions are normally used with continuous dissolution equipment and are less sensitive to Fe^{2+} than powder polymers, where dissolution time is more than one hour.

Note: Polymer solutions made up using distilled or potable water may not truly represent the industrial use.



Bench trials with emulsions

General recommendations

When preparing polymer solutions in the laboratory, all recommendations listed in

the paragraph „*Making the polymer solution*” above are also valid.

Cleaning of equipment which has been in contact with emulsions is long and not

easy, so whenever possible, all equipment to be used for working with emulsion in the lab must be disposable.

Among the items of equipment which can be used, disposable plastic beakers and syringes are highly recommended.

The bottle containing the emulsion must be homogenized by shaking it each time prior to opening it to take a sample. For reliable tests use the same source of water than in the plant.

How to take a sample

For accurate testing and analysis, it is very important that samples be taken correctly. After a long time of storage, as the emulsions have a tendency to settle, samples taken from the top of a tank may be too thin, due to excessive oil, and samples taken from the bottom can be too thick.

It is imperative to take the necessary actions (mainly agitation) to homogenize the product before taking a sample.

Note :

To check if the product is homogeneous, a sample must be taken from the top of the tank and a sample from the bottom. Then measure the viscosity of both samples and if they are the same, the product can be considered as homogeneous. If the viscosities are different, the product must be stirred again.

When the viscosities are the same, the value by itself is not particularly important ; it may differ from the value given from the technical information ; normally up to +/- 50% is acceptable. These viscosities are called bulk viscosities. This bulk viscosity

Typical application tests

All standard applications tests can be made from solutions prepared as above.

This includes flocculation tests (Jar test, Laboratory test for centrifuges, Laboratory

is a parameter which is related to the physical aspect and not related to the performance of the product. The value given on the technical information is an average. It is only used to estimate the characteristics of the pumps that will move the product.

Preparation of solutions

To obtain a good inversion/dissolution, enough shear must be applied at the point of contact between the emulsion and water.

The preferred way is as follows :

- prepare a beaker of the desired quantity of water and stir enough to have a wide vortex ;
- weigh the required quantity of emulsion in a disposable plastic syringe ;
- inject the content of the syringe by turning the jet toward the wall of the vortex.

The time for complete dissolution is 10 min. on average.

For agitation, the most preferred equipment is a mechanical agitator with a variable speed motor fitted with a stainless steel shaft, equipped at the end with approximately 2 cm radius long propeller type blades. In such a situation the speed is at least 500 rpm.

Use of a magnetic stirrer is possible but it is less recommended because the power of the agitation is often weak and, as the viscosity of the solution increases rapidly, it becomes impossible to agitate the solution properly.

test for belt press), tests for paper application, oil field applications, etc.

All procedures for these tests are available on request from **SNF**.

Health, Safety, Environmental Information

The polymer contained in the emulsions has the same toxicity (very low) as the powders.

The free acrylamide content of industrial emulsions is lower than 1000 ppm (0.1%) based on emulsion. For special uses it is possible to produce products with less than 500 ppm (0.05%) of free acrylamide.

The oil is a dearomatised aliphatic hydrocarbon. The flash point of the solvent, alone, is over 105°C. The emulsion has a flash point of over 100°C, but when settled it decreases to 100°C.

The surfactants used have very low toxicity, and are obtained from esters of sorbitol and ethoxylated alcohols.

The cationic emulsions are eye irritants. The degradation of ADAME-based polyacrylamide is ecologically advantageous. Due to hydrolysis, the cationic charge, which represents a risk for aquatic organisms, is not persistent in the aqueous environment. At natural pHs (between 6.0 and 8.0), hydrolysis breaks the ester bond and the

cationic group cleaves off to form an inoffensive, highly biodegradable substance known as choline chloride. On the polymer end, an acid group is formed which is immediately neutralized, forming an anionic polyacrylamide of very low aquatic toxicity. In this way, ester-type polyacrylamide reduces the aquatic toxicity by a factor of 50 in just 12 hours.

Hydrolysis continues until no cationic charge remains. Complete hydrolysis is achieved within 24 hours.

Two major environmental risk assessments on polyelectrolytes used the hydrolysis of ester-type polyacrylamides to conclude that they are not a risk for the environment.

□ „A Review of Polyelectrolytes to Identify Priorities for EQS Development”
United Kingdom Environmental Agency, 1996.

□ „An investigation into the environmental impact of polyelectrolytes in waste water treatment plants” STOWA (Stichting Toegepast Onderzoek Waterbeheer : Netherlands Waste Water Authority), 1995.





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