**Polyacrylamide Emulsions Handbook**

**Table of Contents**

1- **Introduction**

General description of the polyacrylamide emulsions ....................................................... 1-2
Differences between polyacrylamide emulsions and powders ........................................... 1-2
Emulsions are complex liquids ................................................................................................ 1-2

2- **Storage and Handling of Emulsions**

Basic principles .......................................................................................................................... 2-2

Storage and handling of emulsions: list of situations and operations ....................................... 2-2

- Lumps, skins, gels, etc. in the emulsion .................................................................................. 2-2
- Settling ...................................................................................................................................... 2-3
- Color of the emulsions ............................................................................................................ 2-4
- Pumping an emulsion ............................................................................................................ 2-4
- Filtering an emulsion ............................................................................................................... 2-5
- Spills ........................................................................................................................................ 2-6
- Cleaning ..................................................................................................................................... 2-6
- Emulsions exposed to non recommended temperatures ....................................................... 2-7
- Storage ...................................................................................................................................... 2-7
- Compatibility of emulsions with materials ............................................................................. 2-8
- Blends of emulsions ................................................................................................................. 2-10

Dehydrated emulsions ............................................................................................................. 2-10

3- **Polymer Solution in Water Prepared from an Emulsion**

Making the polymer solution .................................................................................................... 3-2

- Fundamentals ......................................................................................................................... 3-2
- Details on the main parameters .............................................................................................. 3-2
  - Water quality - Concentration of solutions ....................................................................... 3-2
  - Shear during inversion - Make-up systems ......................................................................... 3-3

Stability of the polymer solutions ............................................................................................ 3-3

- Generalities ............................................................................................................................. 3-3
- Hydrolysis ............................................................................................................................... 3-3
- How to assess potential hydrolysis and react to limit .......................................................... 3-4
- Free radical chain degradation ............................................................................................. 3-5

Bench trials with emulsions ...................................................................................................... 3-6

- General recommendations ..................................................................................................... 3-6
- Preparations of solutions in laboratory ................................................................................ 3-6
- Typical application tests ......................................................................................................... 3-6

4- **Health, Safety, Environmental Information**

Health, safety, environmental information ............................................................................. 4-2
INTRODUCTION
General description of the polyacrylamide emulsions

Polyacrylamide emulsions are dispersions or suspensions of a hydrogel of water soluble polymer in an oil. They are two phases heterogeneous systems and comprise several components. They are not concentrated polymer solutions. The hydrated polymer is in the shape of microbeads of 1 micron average diameter. These microbeads are dispersed in the hydrocarbon (oil) and stabilized (protected against coagulation or agglomeration) by surfactants. The water proportion varies from 20% to 40% of the final product, depending on the grade. Water is not considered as free; it is one of the polymer gel components.

Polyacrylamides are high molecular weight water soluble or swellable polymers obtained from water soluble monomers (acrylamide, acrylic acid, adam-methyl chloride, etc.) Their main uses are as flocculants in water treatment and mineral processing; drainage and retention aids in the paper industry; thickening agents etc.

SNF produces «self-inverting emulsions only». This means that the polymer can be released in a short time by addition to water, without the need for another chemical.

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 shorter and there are almost no solubility problems.

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

Emulsion of polyacrylamide
STORAGE AND HANDLING OF EMULSIONS:

- BASIC PRINCIPLES
- LIST OF SITUATIONS AND OPERATIONS
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 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:
- In the following paragraphs: emulsion is the commercial product and is a heterogeneous suspension of hydrated polymer in oil. After addition of the emulsion in water, a homogeneous solution of polymer in water is obtained.

- Technical details and information on all equipment described in the following paragraphs are found in the FLOQUIP brochure available on request from SNF or by contacting the Department for engineering of SNF.

Storage and handling of emulsions: list of situations and operations

Lumps, skins, gels etc. in the emulsion

Reasons for observation

Emulsions are filtered at the end of production and are fluid and free of any heterogeneousness when they leave the plant. But during transport or storage in non recommended conditions, situations arise where lumps, skins, gels, etc. can appear in the emulsions.

The more common causes of this problem are:
- emulsions are submitted to very cold or freezing temperatures.
- cycles of warm and cold temperatures are experimented.

Most often this happens when an emulsion is stored outside. These phenomena are sometimes called « raincycle ».

An atypical example of « rain cycle » is described hereafter:

“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 vapor 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.”

Lumps, skins, gels are also observed in case of water contamination or if the container has been left a long time open or when the product has exceeded a long time after the expiration of its lifetime.

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 between 500-1000 microns.

For customers supplied in standard 1 ton 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.
(See “Filtering an emulsion”, below)

Filtration with Floquip SE
Settling

Main observations

Upon 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 the settlement of an emulsion. It depends on the grade, the batch, the temperature of storage and many other parameters.

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

Too strong or too long agitation can provide too much shear to the emulsions and destabilise them.

Agitation by recirculation is not recommended, but in case where there is no other ways, 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 highly dry) is also possible but less recommended.

Small packages recommended by SNF are plastic pails (polyethylene), full opening plastic drums, 1 ton containers (tote-bin, IBC).

For 1 ton containers (tote-bin, IBC) the best way is the use of the Floquip SE.

For other details on agitation see also § «Storage of emulsions» p. 2-7.

After lifetime has expired filtration from container to container is recommended to recover the emulsion.
**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 and some greenish. As emulsions are multi-phase 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 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. Therefore 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**

**What kind of pumps**

**Large flow rates (more than 1 m³/h)**

To pump an emulsion (transfer, unload tanks etc.), use pneumatic pumps, lobe pumps, gear pumps, rotating piston pumps or progressive cavity pumps.

Avoid centrifugal pumps for which there is a problem of breaking the emulsion in the high speed mechanical seal.

**Small flow rates (up to 1 m³/h)**

To pump an emulsion (e.g. to dose or to feed the make-up system for polymer solution preparation) use progressive cavity pumps (Monopump or Moynopump) with a stainless steel rotor and a stator made of Viton or Perbunan.

*Note: With progressive cavity pumps avoid dry running which can damage the stator.*

For very small flow rates (0-3 l/h), it is possible to use diaphragm pumps (but there are sometimes problems of destabilisation of the emulsion) or peristaltic pumps.

Other equipment used when pumping or filtering an emulsion (fitting, valves, pipes) must be designed in accordance to the same recommendations as the pump, and the material used must be chosen by following the guidelines for material compatibility.

For more details on compatibility of emulsions with material see paragraph *Compatibility of emulsion with materials* page 2-8.

Actually, in many locations the equipment is already present and cannot be modified. Very often piston or diaphragm metering pumps are used for dosing the emulsion. In the case of use of these types of pumps, low stroke types are preferable (30 strokes/minute).

In case of other situations SNF advises customers to contact the department for engineering of SNF for more information on equipment for more information.
**Principal difficulties**

The product contains lumps, gels, skins etc.

This can plug the pumps (mostly the small ones). The first operation is to transfer the product. (See the sections above on ‘Lumps, skins, gels etc. in the emulsion’ and ‘Filtering an emulsion’).

*Note: The agglomerates, being water soluble, can be pumped and dissolved with the emulsion itself, except in paper applications where all non totally-dissolved polymer has to be avoided.*

**Strong shear in the pump:**

Any configuration which creates a strong shear in the pump must be avoided. The typical case is when there are check-valves, as in electromagnetic pumps; the shear destabilises and locally coagulates the emulsion on the seats of the closure balls. The bead start to stick, gel appears in the spring and the problem worsen quickly, resulting in a full blockage of the pump.

**Pressure drop in front of the pump:**

This increases the shear in the pump and in the piping in front, resulting in a destabilisation of the emulsion and the formation of gels. It is strongly recommended to avoid:

- any device creating an increase of pressure drop in front of the pump (valves, filters etc.);
- any configuration where the pump injects the emulsion in a pipe in which the pressure is high.

**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 return 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.

**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 2-2.

**How to filter**

SNF recommends to filter through a bag with a large area. Mesh sizes more recommended are 500-1000 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.
Other recommendations

Avoid filtration at mesh size below 500 microns. Avoid use of narrow ways. In line filtration just before use is not recommended. Do not agitate the emulsion before filtration.

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 after a while to a crust stick on the ground which is very difficult to remove even by 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 polymer. In general it is highly recommended to let this film/skin remain as such, or just make a simple 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 : 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.

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.

**Emulsions exposed to non recommended temperatures**

At higher temperatures, above 30°C, the settling is accelerated and the emulsion becomes more difficult to re-homogenize. Sometimes a too long period at a too high temperature leads to complete coagulation.

At temperatures under 5°C the product becomes more and more viscous and difficult to pump.

The emulsions remain normally pumpable until -10°C, but solidify after and cannot be transferred any more. If the emulsion has been frozen, it is possible to restore the product using the same procedures and recommendations as explained in the above paragraphs. In such a case, it is necessary to wait for the product to reach a temperature between 0°C and 30°C. In such a situation, the quantity of lost product (gels retained by filtration) may be not negligible.

In addition, if the emulsion is subjected to freeze-thaw cycles, complete destabilisation can occur.

In any case, when such a bad situation has happened, the restored product is usable but it is likely that the dissolution of the polymer may be affected.

**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, 1 ton containers (tote-bins, 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)

**Storage tank**

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.
Agitation

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

So 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 on short periods. Too strong or too long agitation can provide too much shear to the emulsions and destabilise them.

Typical examples of how to proceed:

- Pails can be shaken 4-5 times by hands 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 mn. a week or 10 mn. 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. before use 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 tons). 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.
The general compatibilities are shown in the following tables:

**PLASTICS**

<table>
<thead>
<tr>
<th>Plastic</th>
<th>ANIONICS</th>
<th>CATIONICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Plasticised PVC (hoses)</td>
<td>very poor</td>
<td>very poor</td>
</tr>
<tr>
<td>Polyethylene high density</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>Polyethylene low density</td>
<td>poor</td>
<td>poor</td>
</tr>
<tr>
<td>Crosslinked polyethylene</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Fluorised polyethylene</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>PTFE</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>PVDF</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>Fiberglass (FRP)</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Polyamide (nylon)</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Plexiglass</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>ABS</td>
<td>medium</td>
<td>medium</td>
</tr>
</tbody>
</table>

Polyethylene is used for the transport 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.

**METALS**

<table>
<thead>
<tr>
<th>Metal</th>
<th>ANIONICS</th>
<th>CATIONICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>very poor</td>
<td>very poor</td>
</tr>
<tr>
<td>Galvanised iron</td>
<td>very poor</td>
<td>very poor</td>
</tr>
<tr>
<td>Stainless steel 304</td>
<td>very good</td>
<td>medium</td>
</tr>
<tr>
<td>Stainless steel 316</td>
<td>very good</td>
<td>medium</td>
</tr>
<tr>
<td>Hastelloy</td>
<td>very good</td>
<td>good</td>
</tr>
<tr>
<td>Steel coated with polyester and glass flakes</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>Aluminium</td>
<td>poor</td>
<td>very poor</td>
</tr>
<tr>
<td>Copper</td>
<td>poor</td>
<td>very poor</td>
</tr>
<tr>
<td>Zinc</td>
<td>very poor</td>
<td>very poor</td>
</tr>
</tbody>
</table>

**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.

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

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 emulsions of SNF are compatible 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, e.g. 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.
POLYMER SOLUTION IN WATER PREPARED FROM AN EMULSION
Making the polymer solution

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 which 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.

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 CaCO₃ 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.

It is therefore possible on site:

- to adjust the high HLB surfactant level in the emulsion product to a level previously determined by testwork on the water to be used.
- small additions of high HLB surfactant to the dissolution water (typically 8 moles ethoxylated alcohol or alternatives) at a level of 2 to 10% on the emulsion itself.

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 is the most recommended. 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.

Note: standard emulsions contain between 28 and 46% active content Optimum dilution is between 50 and 100 fold.
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. If the emulsion is efficiently dispersed, there is no need for further agitation to obtain dissolution, only a contact time of 10/15 minutes is imperative. In practice the inversion is not perfect, a further agitation is necessary in the storage tank for 10/15 minutes.

Due to the two types of agitation necessary for inversion and dissolution, continuous dissolution equipments (Make-up systems) are often preferred.

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.

Anionic emulsions

<table>
<thead>
<tr>
<th>Anionic emulsions have good stability in the range of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Content</td>
</tr>
<tr>
<td>Stability</td>
</tr>
</tbody>
</table>

Cationics emulsions

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

<table>
<thead>
<tr>
<th>Alkalinity</th>
<th>Low</th>
<th>High</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Content</td>
<td>1 g/liter</td>
<td>1 g/liter</td>
<td>5 g/liter</td>
<td>5 g/liter</td>
</tr>
<tr>
<td>Stability</td>
<td>1 hour</td>
<td>10 minutes</td>
<td>8 hours</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Acid Stabilised Emulsion</td>
<td>4 hours</td>
<td>1 hour</td>
<td>2 days</td>
<td>8 hours</td>
</tr>
</tbody>
</table>

Hydrolysis

The main reason for instability of the water polymer solution obtained from cationics 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.

An important case for this hydrolysis to occur is the use of alcaline buffered water to make the solution. In such a situation the time for using the solution can be very short and reach in some cases less than 10 mn. 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.

How to assess potential hydrolysis and react to limit:

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, and most preferred 5.5.

The pH must be measured in the water which will be used industrially.

---

**CATIONIC POLYMER HYDROLYSIS**

V is c o s i t y  ( c e n t i p o i s e s )

With water pH 5.5

With buffered water pH 8°

---

*Decrease of viscosity of cationic polymer solution in water at different pH*
When the pH is below 6, 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 (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, 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;
- use MADAM-methyl chloride polymers.

**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.

**Note:**

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

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 Fe2+ causes chain degradation, aerating the water oxidises it to Fe3+ and so reduces the effect;
- adding a chelating agent before aeration (whenever possible) increases the speed of the oxidation of Fe2+;
- use of an oxidizer such as perborate at 2 to 4% (based on the active polymer) will rapidly oxidize the Fe2+ to Fe3+;
- increasing the dissolution concentration decreases the Fe2+/polymer balance. This is the easiest solution for Fe2+ 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 Fe2+ than powder polymers, where dissolution time is more than one hour.
**Bench trials with emulsions**

**General recommendations**

All recommendations listed in the paragraph ‘Making the polymer solution’ above are valid for the conditions to be followed when preparing the solutions in the laboratory.

Cleaning of equipment which has been in contact with emulsions is long and not easy, so all equipment to be used for working with emulsion in the lab must be disposable, as much as possible. 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 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 to 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:

- 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.

**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 test for belt press...) tests for paper application, oilfield applications etc...

All procedures for these tests are available on request from SNF.
HEALTH,
SAFETY,
ENVIRONMENTAL INFORMATION
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 and 8), 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.
