

PREPARATION OF ORGANIC POLYMERS

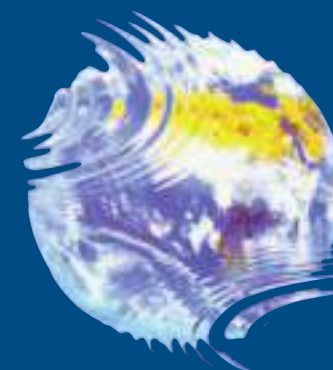


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An in-depth knowledge of the main properties and characteristics of the organic polymers used in water treatment is important for the optimal use of these reagents.

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1 General data on organic coagulants and flocculants

1.1. The coagulants :

There are two main families of coagulants :

- **Mineral coagulants** which are simple metal salts (FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, ...) and polymerized metal salts (PAC, PASS,...).
- **Organic coagulants** which include polyamines, polyDADMACS, dicyandiamide resins and melamine formaldehyde resins.

1.1.1. Characteristics :

The two key characteristics of organic coagulants are :

- **A very high cationic charge density** to neutralize the negative charges present on the surface of the colloidal material.
- **A relatively low molecular weight** to allow good diffusion of the cationic charges around each particle and, due to their low viscosity, good distribution of the coagulant in the effluent.

Organic coagulants are usually in **liquid form** with the exception of polyDADMACS which can also be produced in a solid form (polyDADMAC beads). The viscosity of the liquid form is quite low (< 2 000 centipoises) but can reach 20 000 centipoises with concentrated polyDADMACS.

Concentrations in active material are between 8 and 70% (except for the polyDADMAC beads which are 100% active) with common concentrations between 40 and 50%.

The lowest **molecular weights** are obtained with the dicyandiamide resins (between 3 000 and 150 000) and the highest with the polyDADMAC beads (up to 2 500 000).

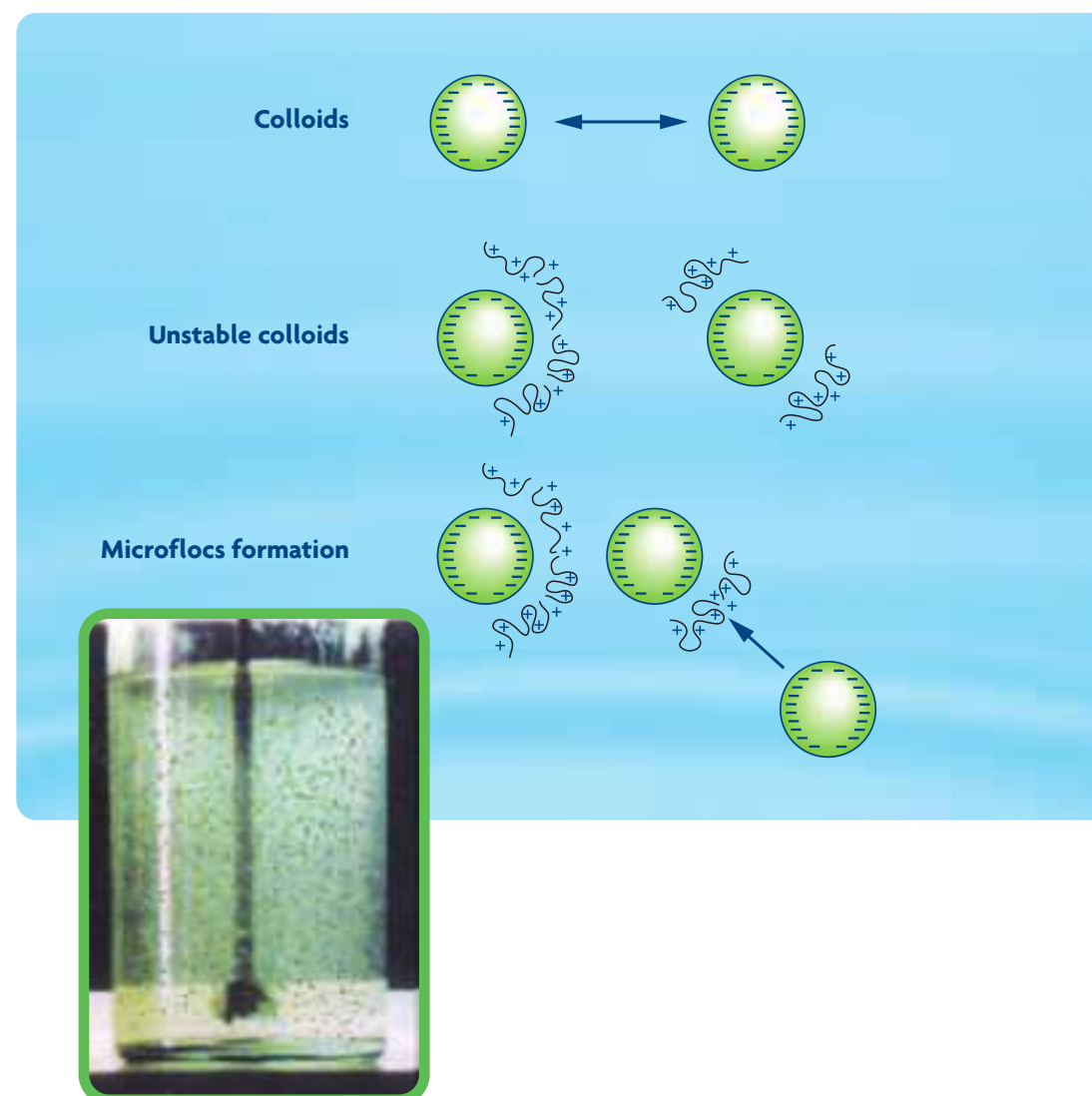
1.1.2. Action :

The coagulants, whether mineral or organic, have active groups : **cationic charges (+)**. These cationic charges offer a high degree of affinity for the surface of very fine and colloidal particles in suspension in the water that are surrounded by opposite electrical charges (-). The cationic charges supplied by the addition of coagulant contribute towards the reduction of the repulsive electrical forces through the **neutralization of the charges around each colloidal particle**.

This neutralization of the charges leads to a destabilization of the very fine particles, which results in an agglomeration of the particles. These agglomerates are then called **flocs** or **microflocs**.

The flocs, which are composed of a large number of elementary particles, will be easier to extract from the treated suspension.

ACTION OF A COAGULANT



PREPARATION OF ORGANIC POLYMERS

1.1.3. Use and dosage :

Coagulants are used **after dilution**. The rate of dilution will depend directly on the parameters of the solution to be treated (concentration, viscosity, ...) and on the application equipment (pump, flow, ...).

Direct injection of the coagulant can be considered, although a **previous dilution between 0.5 and 10%** is recommended.

The **dosage** of the coagulant will be a function of the number of charges to be neutralized in the medium, therefore on the concentration in colloidal particles in the water to be treated.

Other parameters also influence the dosage such as:

- **Agitation** : good dispersion of the coagulant in the solution to be treated is necessary for all the charges surrounding the colloidal particles to be neutralized (Flash mixing with a speed gradient of $1\,000\text{ s}^{-1}$ is recommended).
- **Dilution of the coagulant** : the more the coagulant is diluted, the better the dispersion in the water to be treated and therefore the better neutralization of the charges.

1.2. The Flocculants :

1.2.1. Characteristics :

Organic flocculants differ from coagulants through :

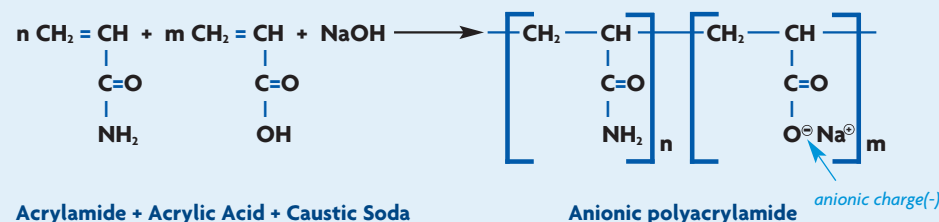
- Their **molecular weight** which is much higher : 3 000 000 to 20 000 000. This allows the flocculant to agglomerate the already destabilized particles.
- An **ionic charge** that varies from 0 to 100 % anionicity (-) or cationicity (+), depending on the effluent to be treated.
- Various **physical forms** : liquid, powder, beads, emulsion, dispersion.

There are two key categories of flocculant :

- **Anionic flocculants** that bring anionic charges (-) into the medium.

NON IONIC AND ANIONIC POLYACRYLAMIDES

Copolymers of acrylamide and acrylic acid



Note : with $m = 0$, the polyacrylamide is non-ionic

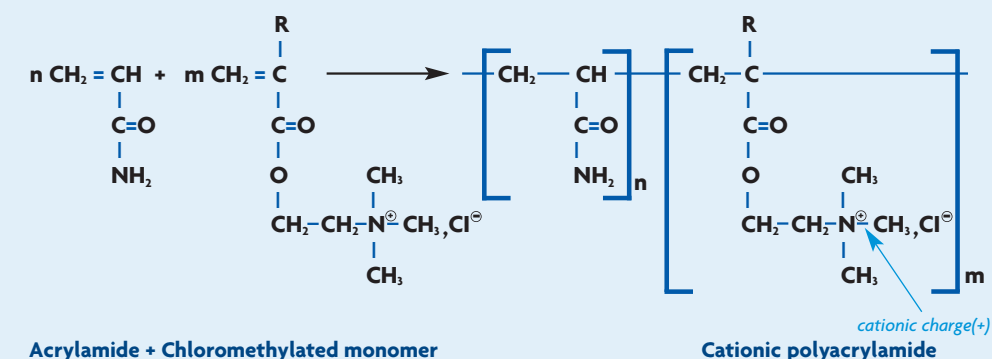
Anionic polyacrylamide

anionic charge(-)

- **Cationic flocculants** that bring cationic charges (+) into the medium.

CATIONIC POLYACRYLAMIDES

Copolymers of acrylamide and of a chloromethylated monomer



Note : with $R = \text{H}$: ADAM (dimethylaminoethyl acrylate)
with $R = \text{CH}_3$: MADAM (dimethylaminoethyl methacrylate)

Different levels (percentages) of **ionic charge** are available : **from 0 to 100%**.

Several commercial forms exist and they come from different methods of polymerization :

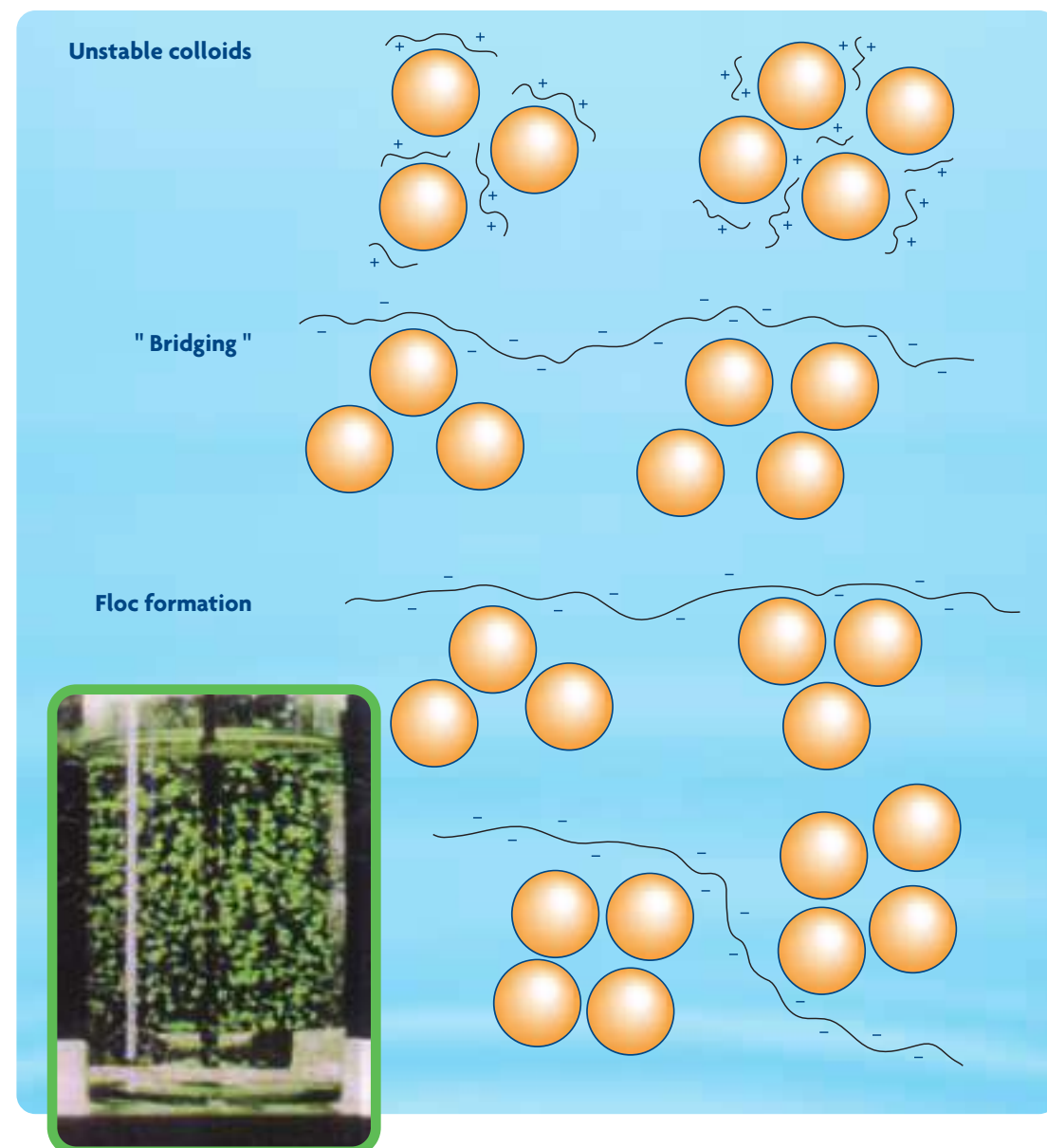
- **Powders** : The monomers are polymerized in a gel form. The gel obtained is then ground and dried. The main advantage of these products is the 100% active matter.
- **Beads** : The monomers are placed in suspension in a solvent and then polymerized. The solvent is then evaporated to obtain microspheres. The main advantages of these products are the absence of dust and rapid dissolution.
- **Emulsions** : The monomers are emulsified in a solvent and then polymerized. At the end of polymerization, a surfactant is added (also called invertor or breaker). It will make the emulsion dilutable in water. The main advantages of these products are their liquid form (easy to use) and an increased efficiency on certain applications (possibility of obtaining specific molecular structures).
- **Liquids** : Monomers are polymerized at low concentration in aqueous solution. The main advantage with these products is the simplicity of use.
- **Dispersions** : The monomers are dispersed in a brine and then polymerized, thus giving a water dispersion with neither solvent nor surfactants. The main advantage of these products is their ability to be directly fed inline without any expensive make-up equipment or aging time. They have also been found efficient in phase separation of flotation processes.

1.2.2. Action :

Once they are in the aqueous solution, the flocculants have active groups : (+) charges or (-) charges. Depending on whether the flocculant is more or less ionic, the interaction with the particles is accomplished through **ionic** or **hydrogen bonds** (e.g. non-ionic polymers). The type and the percentage of electrical charge chosen for flocculation should be tested in the laboratory to insure good results with the types of particles present in the water : mineral, organic, ...

With their very high molecular weight, the flocculants allow the size of the already destabilized particles (coagulated or natural) to be increased and thus **to accelerate the liquid/solid separation**.

FLOCCULATION DIAGRAM



1.2.3. Use and dosage :

The flocculants must be completely dissolved before use. This dissolution depends on the commercial form :

- For products in **solid form** : after good dispersion of each grain separately in the water, agitation for approximately one hour is necessary for reaching maturation. The agitation should be sufficient to maintain the product in suspension, but not too fast thereby avoiding the mechanical degradation of the polymer. After maturation, a uniform, viscous solution should be obtained.
- For **emulsions** : violent agitation is necessary when the emulsion comes into contact with the water. Maturation is quicker and the solution can be used immediately, however an aging time of some 10 minutes is preferable.
- For **liquids** : an in-line dilution with a static mixer is sufficient.
- We recommend **active material** concentrations of **1 g/l for the anionic flocculants** and **3 g/l for the cationic flocculants**. A **post-dilution** is then often set up to facilitate the mixing of the flocculant and the solution to be treated, by reduction of the concentration and therefore of the viscosity of the flocculant solution.

Notes :

- The solutions, even diluted, are extremely viscous. The viscosity of a flocculant solution is mainly linked with its molecular weight.
- Polymers are sensitive to mechanical degradation (agitation).
- The grains tend to agglomerate if they are not correctly dispersed.
- These products spread over damp surface are extremely slippery.
- The dissolution speed of powders is affected by
 - ionicity,
 - particle size,
 - concentration,
 - water temperature.
- Dissolution time for **non-ionic** powder flocculants may reach **4 hours**.
- The solutions of cationic flocculant are not very stable over time (**hydrolysis phenomenon**) due to the hardness of the water and a fresh solution should be prepared each day with a control of the solution's pH. A **pH lower than 5.5** is recommended. All flocculant solutions are sensitive to Fe^{2+} .

2 Laboratory preparation

At laboratory level, the aim is to choose and assess the performances of the polymers on an effluent. An optimal preparation of the polymer solutions will avoid results that cannot be reproduced on an industrial scale.

To prepare small amounts of solution (100 - 200 milliliters), a minimum amount of equipment is necessary :

- **Agitators** : these can be magnetic or mechanical agitators. Their aim is to create an agitation sufficient for dispersing the products in the water.
- **Beakers** : in plastic or glass with a volume of between 200 and 1 000 milliliters.
- **Precision scales** : these should be able to weigh with a precision of 0.001 gram.
- **A spatula and a weighing cap** for products in solid form.
- **Plastic syringes** for injecting products in liquid form.

Preparation of the three main forms is as follows :

2.1. Liquids :



The injection of a coagulant does not require any special precaution since the product is already in aqueous form.



After a thorough agitation, the solution is ready for use in just a few seconds.



The final appearance of the solution should be as follows : no apparent viscosity, translucent (except for the iron salts) and homogeneous.



2.2. Emulsions :



The emulsion is injected into the vortex created by the agitation. In addition, the entire amount of the emulsion should be added as quickly as possible.



After injection, the vortex closes following the increase of viscosity of the solution (See paragraph 3.2 : representation of an inversion)



After 10 minutes, the solution should be viscous, white and homogeneous.

2.3. Powders and beads :



In contrast to emulsions, solid products are added slowly and into the vortex : the aim being to hydrate each grain separately to avoid their agglomeration.



After addition of the solid, the particles, as they become hydrated, tend to swell and become translucent. The vortex closes following the increase in the viscosity.



After 40 minutes agitation for the beads and 60 minutes minimum for the powders, the solution should have an apparent viscosity and no translucent particles (non-dissolved particles of polymer).



3 Industrial preparation

Industrial use depends mainly on the commercial form of the polymers.

3.1. Liquids :

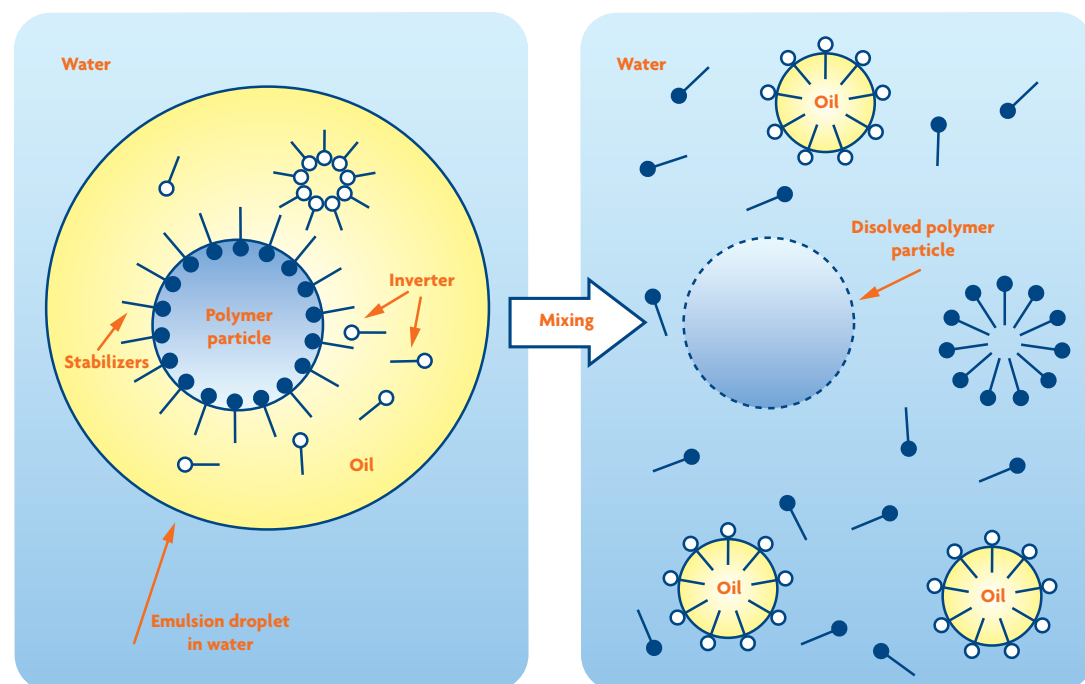
The liquid products such as the organic coagulants and the flocculants resulting from a Mannich reaction require relatively simple equipment. They can easily be pumped and diluted either by **in-line dilution with a static mixer**, or in an **agitated tank**.

3.2. Emulsions :

For the flocculants in emulsion form, simple dilution in water is impossible. Indeed, two phenomena occur during the preparation of a polymer solution obtained from an emulsion :

- An **inversion phase** : the flocculant passes from the continuous oil phase to a continuous water phase.
- A **dissolution phase** : fast.

INVERSION PHASE

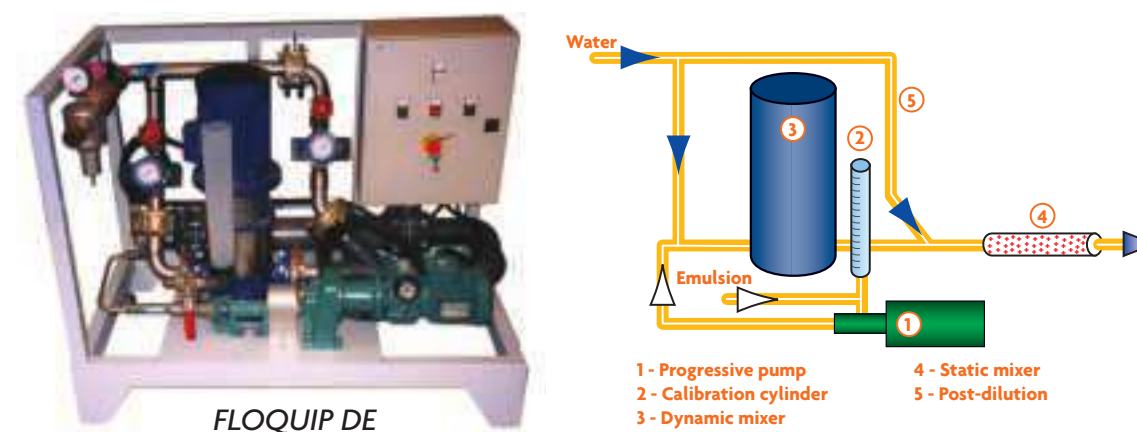


The quality of the inversion/dissolution depends on the following rules :

- The emulsion must be added to water and not the reverse.
- High shear should be applied when the emulsion comes into contact with the water. This prevents the formation of lumps.

Various types of equipment can be found on the market. SNF recommends the use of Floquip DE.

EMULSION MAKE UP UNIT



3.3. Powders and Beads

Solid flocculants require specific equipment for their dissolution with at least one flocculant dispersing device and an agitated tank. In addition, it is important to take into account the maturation time. That is why there are usually at least 2 tanks, with one for dissolution and the other for feeding the solution.

POWDER MAKE UP UNIT



Notes : The equipments shown on this page are basic. More sophisticated make-up unit are available in the Floquip range.

4 Stability and Cleaning

4.1. Stability of the FLOQUAT coagulants and FLOPAM flocculants in their commercial form :

	Liquid Coagulant	Powder/bead Flocculant	Liquid Flocculant	Emulsion Flocculant	Dispersion Flocculant
Stability in months	24	24	12*	6**	3

* Mannich flocculant have a stability of 3 months.

** Dewatered emulsions have a stability of 12 months.

4.2. Stability of the polymer solutions :

It depends directly on the **concentration of the solution** and the **quality of the water** used for dissolution.

4.2.1. For the organic coagulants :

Although they also bring the cationic charges to the medium to be treated, they are significantly less sensitive than the cationic flocculants to hydrolysis.

	Polyamines	PolyDADMAC	Dicyandiamide Resin	Melamine Formaldehyde	PAC	FLB Series
Concentration	1%	1%	1%	1%	1%	1%
Stability frequently observed	less than 24 hours	less than 24 hours	24 hours*	1 hour*	10 minutes	10 minutes

* Depends on pH.

4.2.2. For the anionic flocculants :

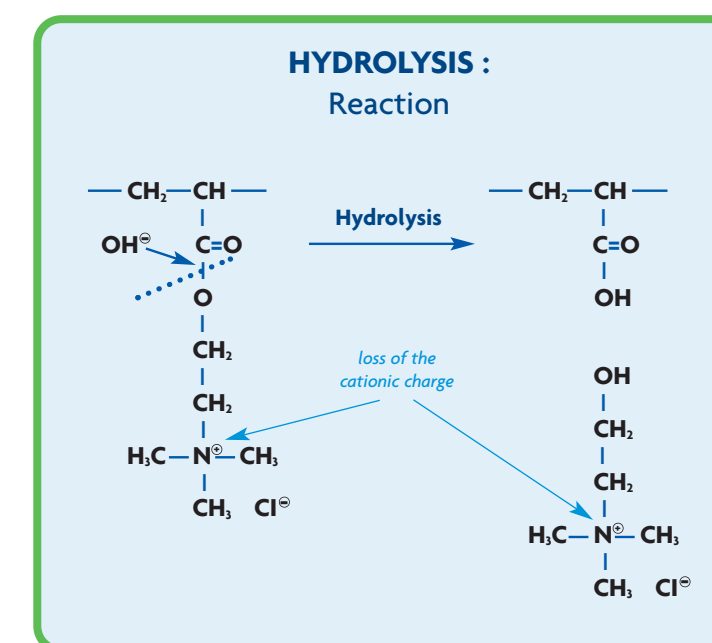
The stability of the anionic flocculant solutions is significantly longer than the cationic flocculant solutions.

	Powder		Emulsion	
Concentration in active material	1 g/l	5 g/l	1 g/l	5 g/l
Stability frequently observed	24 to 48 hours	8 days	8 hours	8 days

4.2.3. For the cationic flocculants :

For the cationic flocculants, the **hydrolysis phenomenon** of the cationic charges occurs as soon as the **pH** of the solution is **higher than 5.5**.

This phenomenon leads to a loss of the cationic charges on the main chain of the polymer.



Anionic charges appear on each monomer having undergone hydrolysis. These charges react with the cationic charges leading to an acceleration in the degradation of the polymer. The performances in application decrease immediately.

To overcome this problem, an **addition of acid** in the flocculant being made is possible to obtain a correct pH after dissolution.
The stability of the cationic polymer solutions therefore depends on the quality of the water used for the dissolution (buffer effect with hard water) :

	SOFT WATER				HARD WATER			
	Powder		Emulsion		Powder		Emulsion	
Concentration in active material	1 g/l	5 g/l	1 g/l	5 g/l	1 g/l	5 g/l	1 g/l	5 g/l
Stability frequently observed without modification of pH	4 hours	24 hours	1 hour	8 hours	50% loss of efficiency	30% loss of efficiency	10 minutes	30 minutes

4.3. Cleaning of the installations :

4.3.1. Commercial form :

For powders and emulsions unintentionally spilled on the floor, it is important to **pick up or wipe up as much as possible** before rinsing with water. Indeed, these products tend to swell when in contact with water, increasing the amount to be cleaned up and, moreover, making the area very slippery and dangerous.

After picking up as much as possible, various reagents can be used to remove the remaining polymer :

- Flopam Cleaning Solution (see specific brochure)
- Bleach.
- Salt.
- Saw dust or absorbers.

4.3.2. Coagulant : commercial form or in solution :

Coagulants, in their commercial form, are already in aqueous solution, therefore rinsing with water is sufficient.

4.3.3. Polymer solution :

Powder and emulsion already in solution (< 20 g/l) present a much easier cleaning problem. **Rinsing the area with water under high pressure** removes all traces of the polymer solution.

Note :

- **Never mix a solution of anionic flocculant with a solution of cationic flocculant.**
A precipitation of the polymers immediately appears in the form of white threads and both solutions are useless for the application.

