



Preparing a Stable Aqueous Suspension from a Powder

Abstract

Aqueous colloids can be stabilised by pH control or by adding dispersants. In this article we set out the steps for making a stable colloid and show how the ZetaProbe and AcoustoSizer can help in this process.

Introduction

To get a meaningful measurement of the size of the particles in a powder it is first necessary to produce a stable dispersion in water. Preparing a suspension from a fine powder usually requires the provision of a dispersing agent and/or the input of considerable energy, normally by stirring vigorously or sonication.

The stirring process pulls the particles apart but they will only stay apart if they repel each other. This will be so if the particles have a big enough electric charge on their surface or if they become coated with dispersing agent.

For clay mineral particles one can often get sufficient dispersion by adjusting the pH to a high value (above pH 10) which gives the particles a high enough surface charge. This also works for most metal oxides, although some, like alumina, may be more dispersed at low pH (pH 4). Sodium hexametaphosphate, or sodium polyphosphate (Calgon) is a suitable dispersing agent for most inorganic materials. Sodium polyacrylate (PAA) (Dispex) is also a common dispersing agent. Both of these are solids readily dissolve in water and they are normally added at around 1% by weight of the solid.

The other large class of dispersing agents consists of the detergents like sodium dodecyl sulfate (SDS) [often (wrongly) referred to as sodium lauryl sulfate].

Dispersing Agents

The International Standards Organization has prepared a detailed report on the procedures required to properly disperse a sample prior to particle size analysis. That report also contains suggestions for suitable dispersing agents for different systems. A sample of material from the report is provided in Tables 1 and 2.

Table 1

Sample Type	Ionic Strength	PH	Suggested Dispersant or Dispersing Conditions
Ionic Salt	< 0.1		Try common ion effect
	> 0.1		Polyion
Metal oxide	< 0.1		Adjust to $\text{pH} < (\text{pH}_{\text{iso}} - 2)$ or $> (\text{pH}_{\text{iso}} + 2)$.
	> 0.1		Polyion
Clay minerals	< 0.1		Adjust to high pH (~ 10). See metal oxide.
Protein			As for metal oxide
Non-polar organic	< 0.1	< 5	Quaternary amine salt
	< 0.1	5 - 8	Organic sulfonate
	< 0.1	> 8	Organic acid salt
	> 0.1		Phospholipid
Low polar organic			Polyionic (polyacrylate)
Organic acid	< 0.1		Adjust pH ($> \text{pK}_a + 2$)
	> 0.1		Phospholipid
Organic amine	< 0.1		Adjust pH ($< \text{pK}_b - 2$)
	> 0.1		Phospholipid
Fluorocarbon			Per-fluoro organic acid

Table 2

Category	Dispersing Agent	Commercial Examples (Manufacturer)
Organic acid(or its alkali salt)		Hystrene (Humkol) Pationic (RITA)
	Salt with triethanolamine	AAS-60S(Vista), Stepanol WAT (Stepan)
	oleic acid sodium dodecanoate sodium linoleate sodium oxalate sodium tartrate PEO/fatty acid	Alkasurf CO(Alkaril), 5430 (Emery)
Organic amine (or amide or quaternary amine halide salt)	Alkylamine	Kemamine T (Humko), Armeen (Akzo) several (Pennwalt)
	PEO/long chain alkylamine	Ethomeen (Akzo) Witcamide (Witco), E Series (Exxon)
	Trimethylalkylamine chloride (or bromide)	Catramide
	PEO/methylalkylamine chloride (or bromide)	Emcol CC (Witco) Ethoquad (Akzo)
	Ethanolamine, triethanolamine 2-amino-2-methyl propanol alkanolamide	Atlas EM-16 (ICI), Monamine (Mona) Witcamide (Witco)
	PEO/alkanolamide	Ethomid (Akzo)
	Imidazoline	Alkaquat (Alkaril), Monateric LF-100 (Mona) Witcamine AL42-12 (Witco)

	amino acid	Lexamine (Inolex)
	Betaine	Aerosol 30 (Cytec) Lexaine (Inolex) Monateric LMAB (Mona)
Organic sulfonate	sodium alkyl sulfonate	Mersolate (R) H, Siponate (R) SA (Alcolac), Ultrawet (R) (Arco) Emulgator (R) 30
	sodium alkylnaphthalene sulfonate	Dispersol (R) T, Perminal (R) BX, Tamol (R) SN, Alkanol (R) (Rohm & Haas)
	sodium alkylbenzene sulfonate	Daxad (R) 23, Ultrawet (R) (Arco), AAS (R) (Vista)
	Isethionate	Igepon (R) AC-78 (GAF)
	sodium dioctyl sulfosuccinate	Aerosol (R) OT (Cytec), Emcol (R) 4000 (Witco)
	Taurate	Igepon (R) T (GAF), Hostapon (R) T (Hoechst)
Perfluoro organic acid	Perfluorooctanoic acid	Zonyl (R) (DuPont), Fluorad (R) (3M), Foralkyl (R) (Atochem)
Phospholipid	Lecithin	Alcolec (R) (American lecithin), Lecithin (Troy)
Polyester /polyacrylate		Elvacite (R) (DuPont), Solsperse (R) (ICI)
Polyionic salt	sodium citrate = $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ sodium hexametaphosphate = $\text{Na}_6(\text{PO}_3)_6$	Calgon (R)
	sodium polyacrylate	LW (R) 300, Dispex (R) 40
		Maypon (R) (Stepan), SuperPro (R)

	sodium silicate sodium tetrapyrophosphate = $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ sodium tripolyphosphate = $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	(Stepan) (?Here or in next slot?) Note: Any alkali metal ion or ammonium may be used in place of sodium
water-soluble organic	Polyacrylate	Darvan (R) C (Vanderbilt)
	Formaldehyde-naphthalene sulfonate	Daxad (R) (Grace), Blancol (R) N (GAF), Tamol (R) N Micro (Rohm & Haas)
	Sulfonated lignin	Polyfon (R) (Westvaco) Marasperse (R) (Reed Lignin)
	tannic acid	Durtan (R) (Durkee)
	sorbitan laurate	Sapan (R) 20 (ICI)
	tall oil acid salts	Polyfac (R) MT (Westvaco)

Finding a Suitable Dispersing Agent

Go to Table 1 first and find the sample type which best fits your material. Note also the concentration conditions represented by the ionic strength. If the salt concentration is low it is usually easier to promote dispersion. If it is high (above 0.1 M) then you will probably have to use a polymeric dispersant.

The first entry in Table 1 (common ion effect) refers to the possibility of dispersing say, silver bromide with either silver ions or bromide ions, which are special ions for that particular surface. That can be done for a few important sols but is not a common procedure.

Consult Table 2 to find a suitable dispersant for your material in water. Proprietary names are given there to help with your selection.

The Dispersion Process

The powder should first be wetted with some water containing the dispersing agent. Mix it around a bit to make sure that the liquid is making contact with all of the solid. Then it can be diluted to a suitable concentration.

Normal samples can be mixed well with a high-speed stirrer, until they appear to be thoroughly homogeneous. Some hydrophobic organic materials may not respond well to this treatment, for high speed stirring may entrain large numbers of air bubbles to which the particles become attached. They will then float to the surface and be difficult to disperse. In this case you must avoid the production of a vortex in the mixing process by using a lower mixing speed.

It is important to make sure that the material which has settled to the bottom of the container is properly mixed in with the rest. A highly dispersed sample of dense material can produce a sediment which is very difficult to redisperse simply by stirring, no matter how vigorously that is done. It may well be necessary to dig the sediment out and wet it up from the paste before returning it to the remainder for the final stirring.

An ultrasonic bath or an ultrasonic probe can help with the dispersion process and may be less destructive for some systems. Ultrasonication is a routine procedure for obtaining dispersion and for thoroughly redispersing a sample that may have been left standing in the lab for some time. However, you should be aware that it can produce chemical by-products which could affect your sample. It should not be used for long periods. A few minutes should normally be enough. After such treatment the sample should be ready for the AcoustoSizer or ZetaProbe. You can establish that the suspension is stable by checking that several successive measurements give the same reading for the zeta potential. If it is not then you will need to stabilise the suspension either by controlling pH or by adding dispersant.

If you do not want to use "artificial" dispersing agents, like Dispex and Calgon or the detergents, then you should try and stabilise the suspension by adjusting the pH. To do this, add some acid or base to adjust the pH while measuring the zeta potential in the "datalogging" mode, to see which direction the pH should be changed to increase the zeta potential magnitude. Continue to add acid or base to increase zeta until the reported zeta does not vary from one measurement to the next. At this stage the suspension will look homogeneous, with no sign of the particle clouds that are evident in the unstable state.

Once the suspension is stable, you can begin refining the dispersion procedure for this colloid by getting a clearer picture of how its zeta potential depends on pH. Put acid or base in the computer controlled syringes (using the Burette Control option in the software) and titrate the suspension from one pH extreme to the other (usually the titrations run between pH 4 and 10). This will allow you to locate the isoelectric point of the sample. Usually the colloid will be stable at 2 pH units above or below the iep (see table 1), but you do not need to be guided by this rule of thumb, for the stability can be assessed by the reproducibility of successive measurements in the ZetaProbe. In the AcoustoSizer you can also look at the drop off in particle size away from the iep. It is only when the suspension is stable that the true particle size can be determined, for in an unstable suspension the measured size is related to the floc size and this depends on factors such as the stirring rate.

If you choose to add some dispersant to the colloid, then you can use the ZetaProbe and AcoustoSizer II to determine how much dispersant is needed. Nearly all dispersants, including the nonionic ones, alter the reported zeta potential. Thus zeta potential measurements can be used in monitoring the dispersant addition. Usually the "optimum" dose is determined by adding dispersant until the zeta levels off and doesn't change with further additions. There is no point in adding any more dispersant than this since it is not going on the particle surface. See reference [1] for examples of this method of dispersant control.

If, for some reason, the sample is too fragile to be treated so vigorously, the initial stirring can be replaced by a roller mixer. In that case you may have to allow several days of mixing

to get the system reasonably dispersed, and it may never occur if the particles are too strongly bonded.

References

1. Greenwood, R. (2003) "Review of the measurement of zeta potentials in concentrated aqueous suspensions using electroacoustics" *Advances In Colloid And Interface Science* **106** 55-81