

## Possibilities of adjusting the plasticity by using the various action principles of additives

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## **1. Introduction**

*"Plasticity is like honesty: something indefinable but which has certain characteristics associated with it."*

In this quotation, Scott Blair succinctly defines the many facets of the relationship. If one attempts to describe or even influence the phenomenon of plasticity, it is of the utmost importance to first find and use a more exact definition in order to plasticize the bodies used in plastic shaping as optimal as possible.

The generally accepted definition of plasticity as a property of solid bodies under the influence of outside forces to create a flowing effect, leading to a remaining deformation when the forces are removed, is applicable for all plastic bodies that are to be shaped. From this point of view of influencing plasticity, however, a clear differentiation between the body to be processed and the shaping method to be used has to be made.

The applied shaping processes differentiate themselves with respect to:

- shaping speed
- shaping forces with respect to water content and the clay mineral proportion
- component geometry
- necessary machinery effort
- use of additives

The bodies to be processed can be naturally occurring plastic (mouldable) or non-plastic bodies. A further differentiating feature is the processing moisture.

Once the influencing factors on the material property plasticity and their differences due to the various raw materials and shaping processes are known, it is fundamentally possible to optimise the naturally plastic bodies, or to give originally non-plastic bodies the ability to be plastically moulded.

A clear differentiation of the bodies to be shaped as well as the shaping processes to be used serves as the starting point for the study. Knowing the chemical and physical mode of operation the resulting pre-requisites allow a decision for the use of additives and their optimal selection.

## **2. Characterization of the bodies and shaping methods**

### **2.1. Characterization of the bodies**

All bodies to be examined have in common their availability as material mixtures with water as fluid phase. With such a basis, the following influencing factors must be considered for plastic shaping:

- type and content of the solid parts
- content of the fluid part
- particle size and particle size distribution
- particle (granule) shape
- surface layer of ions
- deformation, compaction and their speed rate

Depending on the material and the required amount of water for the specific shaping process, the influence of the named factors on the technological steps of the shaping process is to be evaluated differently.

The amount of the fluid phase for the observed range of shaping with plastic characteristics to be examined lies between approx. 2 and 35 mass-%, depending on the process.

The classification of the materials is given as follows [1]:

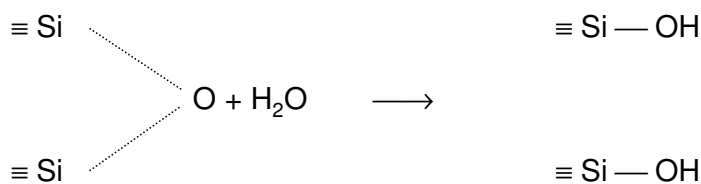
- silicate ceramic materials
  - clay ceramic materials (e.g. roofing tiles)
  - other silicate ceramic materials (e.g. cordierite)
- oxidic materials (e.g. alumina)
- non-oxidic materials (e.g. silicon carbide)

## 2.2. Characterization of the raw material surfaces

Examining the grain surfaces in silicate ceramic, oxide ceramic and non-oxide ceramic bodies as interfaces between solid bodies and water as the surrounding fluid phase, it is assumed that the ions in the outer layer of the solid body must be deformable due to their unsaturated bonding condition for charge compensation.

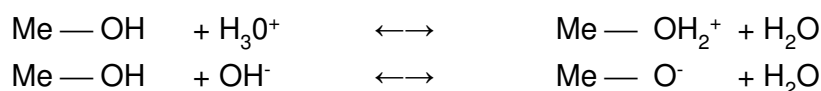
Since a rearranging process to achieve charge neutrality is only very limitedly possible, this compensation in an aqueous system is achieved through the accumulation of H<sub>2</sub>O molecules. Examinations of the raw materials show that the outer layer is built up of O<sup>2-</sup>-ions, since, when compared to cations, they are easier to deform because of their greater polarising ability. These ions come either from the formation of the crystal itself or from an adsorption of oxygen from the atmosphere, through which the initial saturation through adsorption first results.

When in contact with water, for example, the following chemical reaction results for a metal ion Me=Si<sup>4+</sup>:



In addition to the charge that exists on the surface of the solid particle as a result of an interface, new surfaces occur by mechanical destruction of the solid particle. The bonds freed after breakage have a strong need to be saturated. The same chemical reaction results with the difference that the bond between the metal ions (e.g. Si) and the oxygen is partially split due to the effects of forces from outside.

From this, the interactions between the ceramic particles, water and chemical additives, which are all dependent upon the pH-value, result as shown in the following. [2]



### 2.3. Characterization of the shaping processes

The shaping processes for which plastic characteristics are required in a broader sense are classified as follows:

- uniaxial pressing
  - dry (2 - 6% moisture)
  - semi-wet (5 - 9% moisture)
  - wet (8 - 22% moisture)
- isostatic pressing
- extrusion

Fig. 1 shows the existing multi-level interactions between the shaping process, body composition and factors influencing the plastic deformation.

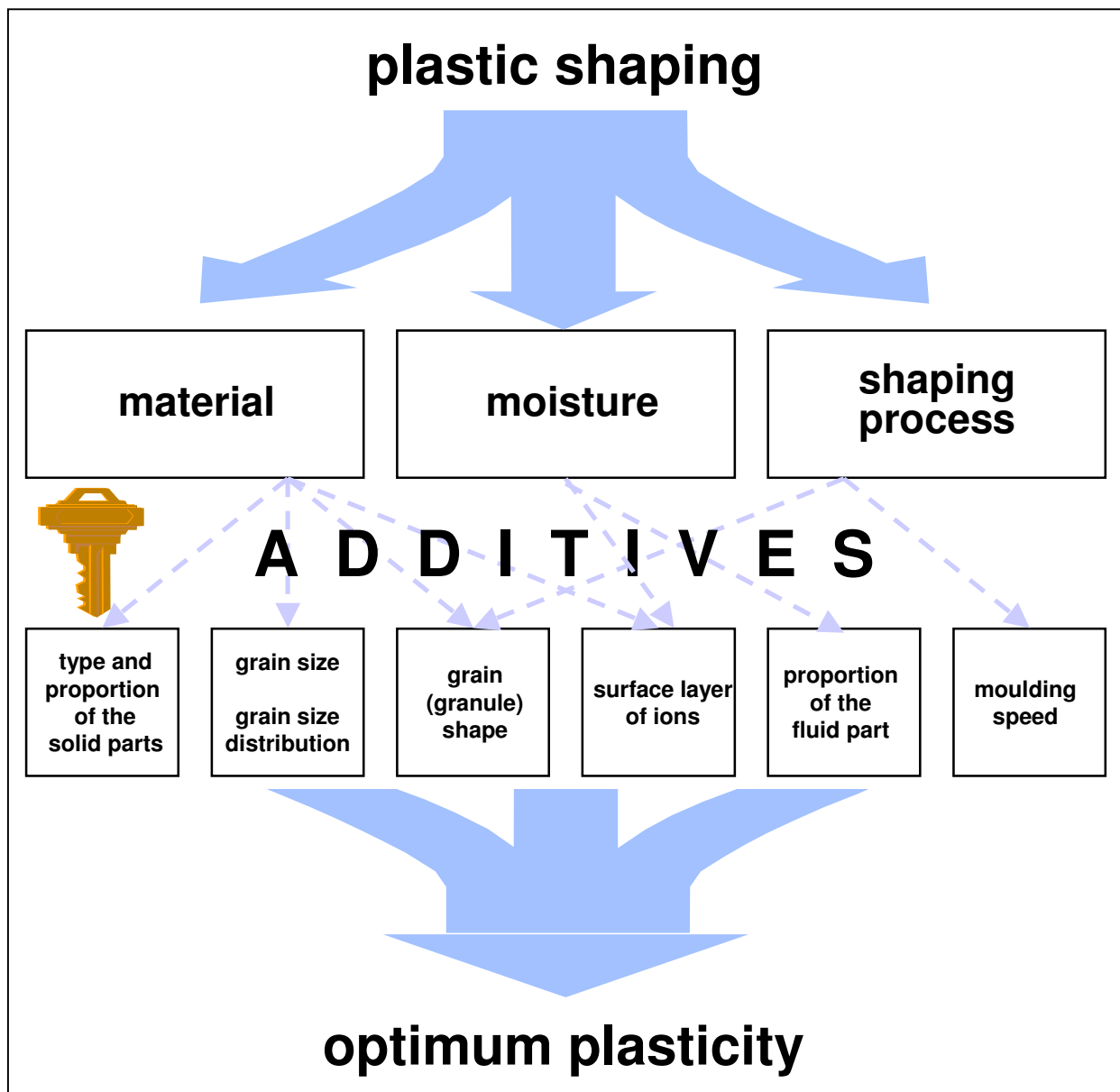


Fig. 1: Interactions between the shaping factors and plasticity

### **3. Function of plasticizing additives**

Depending upon the combination of material, processing moisture and shaping process, different requirements result regarding the mode of action for the additives to be used. In many applications the use of additives is absolutely necessary in order to make shaping possible at all. For others, the processing characteristics of the bodies and thus the properties of the finished product can be optimised with the help of additives.

Plasticizing effects can be brought about through the use of swelling agents, lubricants, wetting agents, pressing agents, temporary binders as well as releasing agents.

The influence on the body can be as follows:

- swelling (swelling agents, temporary binders)
- lubricating
  - within the body (pressing agents)
  - between the body and the mould (lubricants, releasing agents)
- wetting (wetting agents)

In many cases the positive influence of the additive is a result of the simultaneous appearance of many effects.

Using a number of application examples for the production of ceramic products, the various functions of the additives for shaping with respect to their plasticizing properties shall be seen in the following.

#### **Kiln furniture**

Material: silicon carbide  
 Shaping process: uniaxial pressing - dry  
 Aim: optimisation of the plasticity:  
 improvement of the free-flowing properties  
 optimisation of the mould filling behaviour  
 reduction of the density gradient  
 Function of the additives: pressing agent

#### **Roofing tiles**

Material: clay ceramic body  
 Shaping process: uniaxial pressing - semi-wet / wet  
 Aim: optimisation of the plasticity:  
 plasticizing by reducing the mixing water;  
 in other words, achieving the same plasticity with lower moisture  
 Function of the additives: wetting agent

#### **Insulators for electrotechnics**

Material: cordierite / steatite  
 Shaping process: uniaxial pressing - wet  
 Aim: optimisation of the plasticity:  
 improved flow under pressure leading to optimal contour sharpness,  
 as well as a reduction of the density gradient  
 and a reduction in the adhesion tendency to the upper and lower punch  
 Function of the additives: pressing agent / releasing agent

### **Alumina porcelain**

Material:	silicate ceramics or oxide ceramics
Shaping process:	isostatic pressing
Aim:	optimisation of the plasticity: reduction of the density gradient, stress-free pressing
Function of the additives:	swelling agent / pressing agent

### **Rollers for fast-firing furnaces**

Material:	alumina
Shaping process:	extrusion
Aim:	creating of plastic properties: shape stability through to drying / sintering, extrusion free of warpage, creation of a smooth surface
Function of the additives:	swelling agent / lubricant / releasing agent

## **4. Mode of action of plasticizing additives**

The additives used in plastic shaping achieve results that are appropriate for the complex requirements of this shaping technology through the type of contact with the particle surface and through their intrinsically caused operation.

Plasticizing effects can be achieved by the functional groups polyethers, polymer alcohols, and fatty acid preparations. Based on their application, these functional groups operate in the additive groups swelling agents, lubricants, wetting agents, pressing agents, temporary binders and releasing agents.

### **4.1. Description of the functional groups**

#### *4.1.1. Polyethers*

Polyethers (e.g. polyethylene glycol = PEG) possess the ability of non-ionic substances to attract water molecules by their adjacent valences. This is based on the structure of the ether group -C -O -C - which is regularly found.

The adjacent valences are formed by the etherification of the monomers and can be saturated by the accumulation of water. In the example shown, it assumes an association between the O-atom of the ether group of the PEG with the H<sup>+</sup> - ion of the Me-OH-surface group of the raw material particle (Fig. 2). This results in particles having similar charges which repel one another, allowing a slight moving away from one another.

The property of these additives allows a shell to form after the accumulation on the particle surface, fulfilling the effect of masking the morphology. That means that deviating surface structures of the particle from that of an ideal crystal (e.g., indentations or projections) no longer can cause an overlapping or a mechanical bond between the particles. Thus, the particles whose surfaces have been modified can glide more easily when outside forces are applied.

Depending on the average molecular mass, water also accumulates in the polymer, causing swelling. The greater the molecular mass, the stronger the swelling effect.

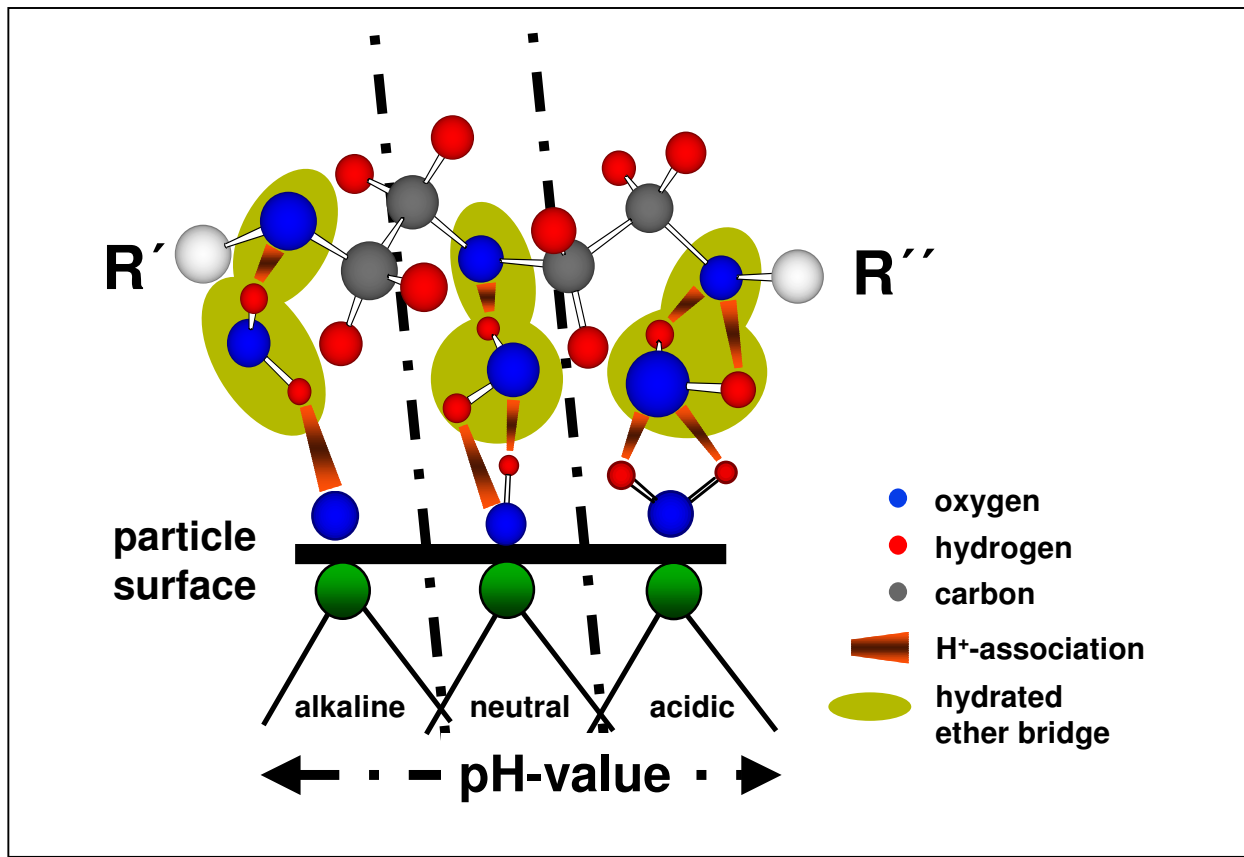


Fig. 2: Interaction polyether / ceramic particle surface

#### 4.1.2. Polymer alcohols

Polymer alcohols (e.g. polyvinyl alcohol = PVA) make their OH group (hydroxyl group) available as a reaction partner, which reacts with the  $H^+$  -ion on the Me -OH surface group of the ceramic particle. The results are once again similarly charged particles that repel one another, and thus can easier glide by one another.

In a similar manner to the functional group polyethers a masking of the morphology occurs, and a swelling effect takes place in polymer alcohols having higher molecular mass due to the accumulation of water.

#### 4.1.3. Fatty acid preparations

The functional group of fatty acid preparations is used in emulsified (water mixable) and non-emulsified (water insoluble) form.

For emulsified fatty acid preparations, the association of the  $H^+$  -ions on the surface of the particles takes place either with ether groups  $-C-O-C-$ , which are available through the emulsifier, or with carboxyl groups  $-COOH$  of the additive (Fig. 3). In non-emulsified preparations, the association of the  $H^+$  -ions only occurs with the carboxyl groups.

The optimised functionality of the emulsified fatty acid preparations is based upon the fact that the emulsifier creates an additional contact possibility to the particle surface through its hydrophilic character. The hydrophobic residual fat causes a separating effect to the neighbouring modified particle. The particles can thus be pushed against each other under reduced effort.

Furthermore, due to its hydrophobic character, the residues  $R'$  of the fatty acid preparations act lubricating on the shell's surface.

And, as in the other functional groups, they have a smoothing effect on the surface by masking the morphology.

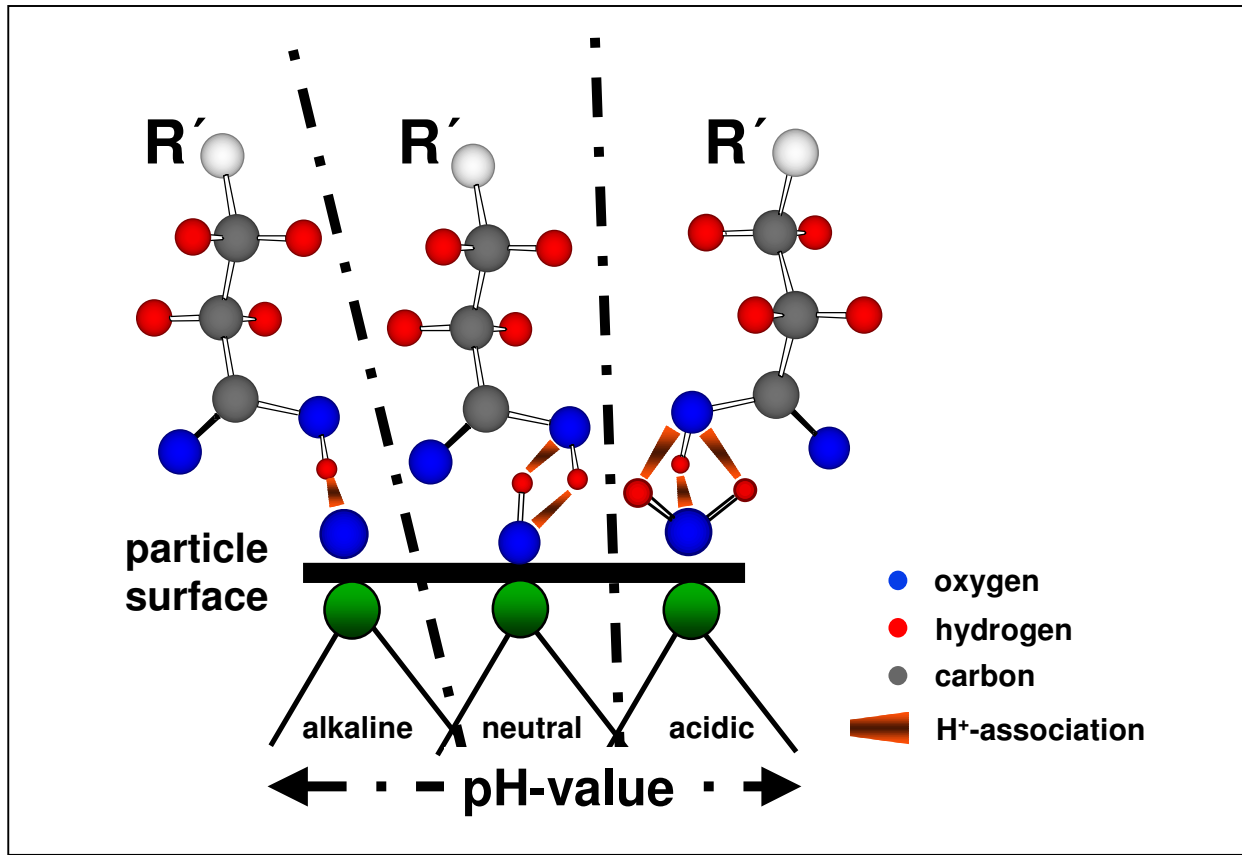


Fig. 3: Interaction fatty acid / ceramic particle surface

## 4.2. Description of the additive groups

### 4.2.1. Swelling agents

In this additive group, not only the raw materials of the function groups polyethers and polymer alcohols come into use, but also the raw materials that contain the functions of both groups. Belonging to the latter group are polysaccharides and cellulose derivatives.

In this conjunction, the special effectivity of carboxymethyl cellulose (CMC) should be noted.

The carboxyl group  $\text{-COOH}$  interacts with the surface of the particle so that it reacts by using hydrogen bridge bonds with the surface groups of the particles. The free OH-groups of the cellulose molecules accumulate water molecules, just like those of the polymer alcohols.

### 4.2.2. Lubricants

Raw material basis for this additive group are polyethers and fatty acid preparations.

The purpose of lubricants is, in particular, to form a gliding layer between the mould wall and the ceramic body.

These additives are used particularly in the extrusion process, where a releasing effect between the body and the die is asked.

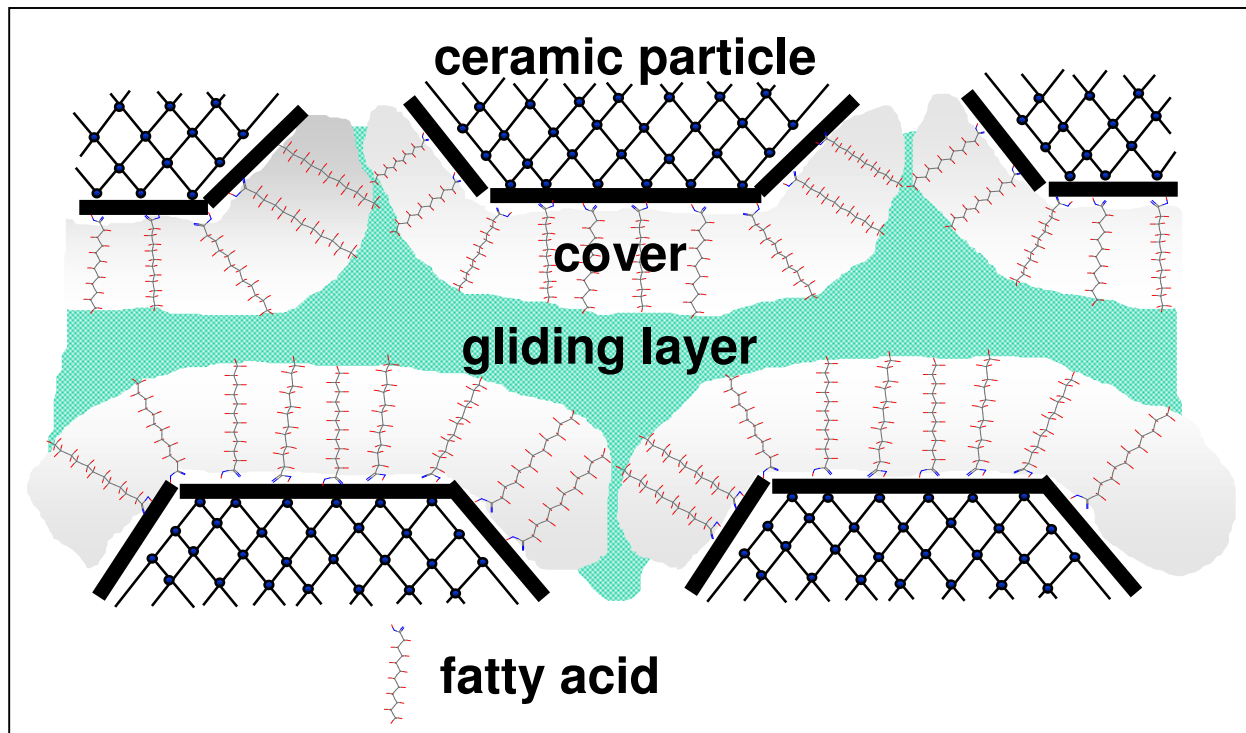


Fig. 4: Mode of action of pressing aids

#### 4.2.3. Pressing agents

The products in this additive group operate similar to those in the lubricants. In contrast to lubricants, however, pressing agents primarily assist in the formation of gliding layers between the raw material particles; i.e. within the ceramic body (Fig. 4).

Fatty acids as well as polyethers are the raw material basis for this group of additives. The fatty acids are made emulsifiable through a reaction with, e.g., ethylene oxide.

#### 4.2.4. Wetting agents

Wetting agents reduce the surface tension of the water and thus lead to a better wetting of the ceramic particles by enlarging the fluid's surface. An optimised homogenization of the body requiring less mixing water because better accumulation of the water results.

Wetting agents are almost always tensio-active products; i.e., either anionic, cationic, or non-ionic surface active substances. These materials are formed out of a hydrophobic molecule R' (e.g. residues of alkyls or aryls) and the hydrophilic operational groups.

They are classified in anionic (e.g., sulfonate, sulphate, carboxylate groups), cationic (e.g., quaternary amine groups), and non-ionic (e.g., polyalcohol residues, polyols, polyethers) groups. The selection of the operational group is oriented on the surface charge of the ceramic particles. The selection of the remaining molecules is a result of the strength of the repelling action of the modified particles, which is achieved through the markedly hydrophobic behaviour.

Furthermore, wetting agents can be conditioned so that they have the ability to exchange ions while at the same time acting as a complex builder, immobilising the higher valence cations that are dissolved in the aqueous solution.

#### 4.2.5. Temporary binders

Additives from this group are created on a polymer alcohol or polysaccharide basis for the individual application. In addition to their adhesive action, they can also act as lubricants as well as creating swelling and thus plasticizing effects due to their formation and molar mass. The contacts of the individual raw materials to the particles' surfaces, and their action as an initiator for the creation of gliding layers between the particles has already been explained above.

Also used are lignin sulfonates. Here the lignin acts as a hydrophobic molecule and the sulfonate group as the hydrophilic group, which is surface active.

#### 4.2.6. Releasing agents

Fatty acid preparations form the raw material basis of this additive group.

The purpose of releasing agents is primarily the formation of gliding layers between the mould and the ceramic body by preventing adherence. In contrast to lubricants, the main area of use is in uniaxial pressing.

### 5. Summary

Blair's introductory quotation about plasticity requires a more precise better definition with respect to the noted "specific properties". The already generally accepted definition describes plasticity as a property of solid bodies to show a flowing effect when acted upon by outside forces. These flowing effects are nothing more than the ability to push the ceramic particles away from one another. Generally, the surface of the particle with respect to the formation of gliding layers is influenced, which makes the pushing away easier. These gliding layers are formed by the creation of a charge compensation on the ceramic particle surface. The charge compensation is the result of the reaction between a charged particle surface and operational groups of the additives. This occurs depending on the pH-value of the ceramic body. A cationic particle surface in an aqueous system is represented by the H<sup>+</sup>-ions of the Me -OH surface group.

The operational groups of the additives are different, depending on the raw material basis:

- |  |  |
|--|--|
| • Polyether:                               | O -atom of the ether groups – C – O – C –            |
| • Polymer alcohols:                        | hydroxyl groups – OH                                 |
| • Fatty acid preparations, non-emulsified: | carboxyl groups –COOH                                |
| • Fatty acid preparations, emulsified :    | carboxyl groups –COOH and ether groups – C – O – C – |

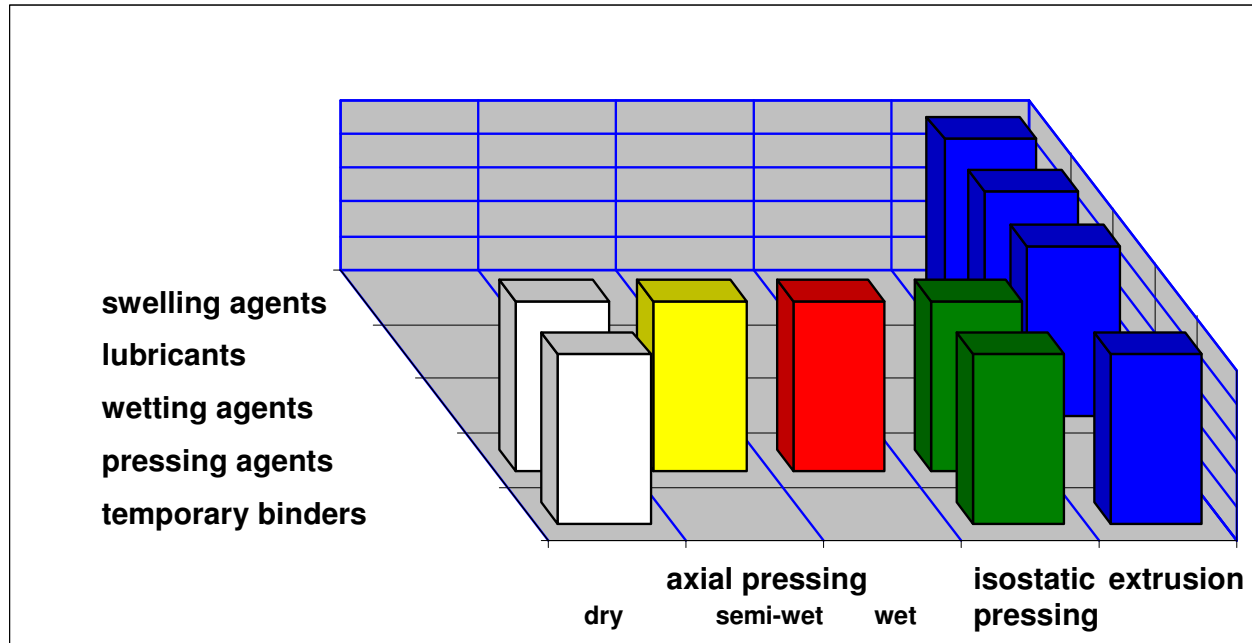
In addition, the possibility exists for swelling in the function groups of polyethers and polymer alcohols, depending upon the molar mass, through the additional accumulation of water in the polymers.

The criterion for selecting the appropriate additive is, in addition to the composition of the ceramic body and the shaping process, the aim of plasticizing.

In this regard, the influences on the repelling ability and thus the shaping ability in connection to improved moulding and product properties can essentially be classified as follows:

- Creation of plastic shaping ability  
e.g., for extruding Al<sub>2</sub>O<sub>3</sub>,  
primarily with the aid of swelling and lubricating effects
- Deformation with less effort required  
e.g. in uniaxial pressing,  
primarily with the aid of lubricating effects
- Achieving good shaping ability using less water  
e.g., reduction of mixing water in roofing tile bodies,  
primarily with the aid of wetting effects

The application profile shown in Fig. 5 once again makes clear the multiple possibilities for using plasticizing additives, which result from the various achievable effects.



**Fig. 5: Application profile for the application possibilities of plasticizing additives**

For the given items shaping processes, ceramic raw materials as well as the aim of plasticizing the required "specific" properties in an optimal plasticizing procedure with reproducible good properties in the end product, are achievable with the help of the correctly chosen additives and additive combinations.

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