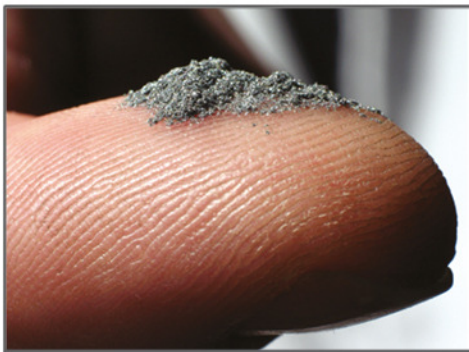
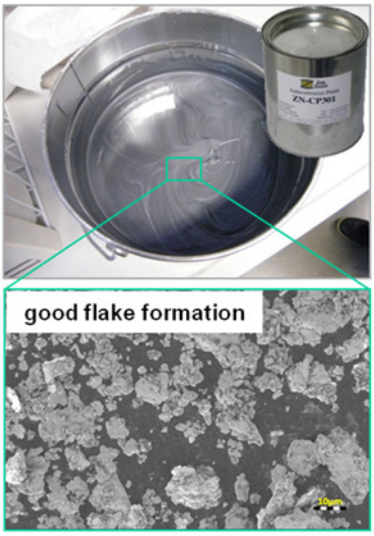


Zoz Group

HKP-ZFP | ZincFlakeCoating ZN-CP301

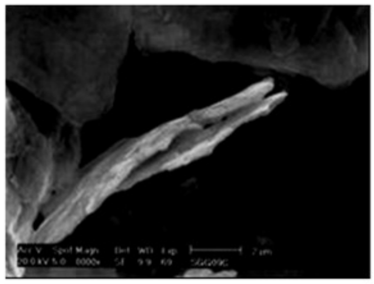
nanostructured Zinc Flake pigments and corrosion protection
high corrosion resistance, easy handling,
saving VOC, CO2, processing time and transportation

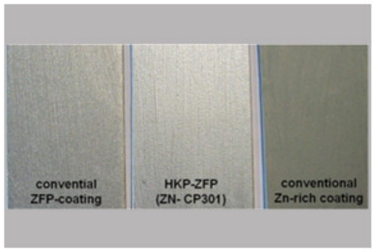


EVONIK INDUSTRIES
Hochschule Niederrhein University of Applied Sciences
Chemie Faculty of Chemistry
Zoz Group
Bundesministerium für Wirtschaft und Energie
impulse ZIM Zentrales Innovationsprogramm Mittelstand

PRO INNO II-project-no. 0078402WZ7
und ZIM-project-no. 2435404SU2

coming up next:
water-based corrosion protection systems with zinc flake pigments

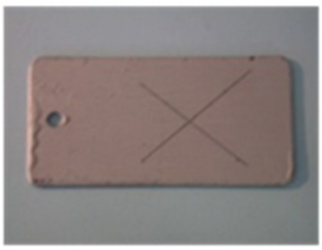




cost-effective high-performance stir-in-Zinc-Flake pigments (ZFP) by High Kinetic Processing (HKP)

commercial ZFP after salt spray test






Zoz-ZFP ZN-CP301 after salt spray test

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HKP-Zinc flake pigments │ Zinc-coating ZN-CP301

Nanostructured zinc flake pigments and corrosion protection
high corrosion resistance, easy handling,
saving of VOC, CO2, processing time and transports

Introduction

In the late 1990s, Zoz was virtually pushed and taken by a still today very important customer to the challenge, that "High Kinetic Processing" (HKP) in the manufacturing of ductile metal flakes (DMF), provides amazing results [1]-[4]. HKP is the synonym for High Energy Milling (HEM), Mechanical Alloying (MA) and Reactive Milling (RM) and describes today's main business area of Zoz. The potential that HKP offers in the generation of DMFs in here is enormous.
Ductile metal flakes by means of the "HEM-effect" due to the high kinetic energy impact (mostly collision of grinding media) can be manufactured up to 1000x faster than in the conventional processing route (classic ball milling or stamping) at significantly lower energy impact (ball milling: mostly shear and friction interaction by grinding media). By the "MA-effect", a whole range of alloys can be in situ synthesized and by the "RM effect", finally also chemical reactions can be utilized on purpose.


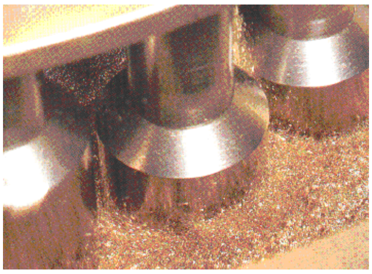


Fig. 1a-c: conventional Zoz-drum(ball)mill with double-sieve tower (special-flake-sieving) for zinc-flake manufacturing, brass flakes in stamping process (Fukuda Metal Foil & Powder Co. Ltd.) and HKP plants Simoloyer® CM08 / 20 (Chemplate Ind.) / 100 (Zoz Technology Center)

The mentioned "classic ball milling" has been and still today is indeed occupied and served from Zoz as its virtually oldest business field (manufacturing of drum-ball mills, roller- and laboratory mills, sieving equipment etc.), however, until about 1990, Zoz activities were limited to the corresponding equipment manufacturing. By starting into - and one also may say due to fundamental innovation of HKP with the Zoz-Simoloyer® technology in recent decades, Zoz beyond equipment manufacturing became a global player for nanostructured materials, where e. g. by solid state synthesis also completely new materials can be and are produced.

By means of such solid-state synthesis e. g. from zinc dust and a minor fraction of aluminum powder, compared to a conventional zinc flake, a brighter and shinier Zn-Al flake can be processed [5]. Intended color change can also result in black zinc flakes [5], functionalization such as e. g. Zn-Ni or Ag-Cu flakes [6] can lead to better corrosion resistance and/or improved conductivity e. g. for EMI shielding or micro soldering. Also in the field of composites, this technology is virtually unlimited. Thus e. g. carbon nanotubes (CNT), ceramic hard phases and/or polymers can be incorporated on nanoscale and result into composites such as Al-CNT, Cu-SiC, Al-PTFE [7]. Since HKP basically represents a "dry" process where most frequently solvents for the process itself are not necessary, HKP can also be regarded as particularly environmentally friendly.

Why zinc flakes, why zinc?

The manufacturing of DMFs at Zoz began as an extensive customer demonstration with Ag- and Cu-flakes. Then there followed a flake generation of all kind of metal, metal-polymer and metal-ceramic compounds. After silver and copper, aluminum was in the top rank of optical function-carrier/pigments. At extremely high market prices, here also extremely complex and time-consuming approval procedures were res. are required, e. g. when it comes to metallic paints for the automotive industry here.

Although under the impression of very promising Al-flake results, Zoz had to realize to be moving towards a comparatively monopolized market as a newcomer. In the end it seemed anyway more promising, to not to deal with as in this case high morphological requirements to "optical effect" materials but better be limited to the massive and particularly rapid change in geometry. Consequently the way to zinc was not far since here a cost-effective generation and formation of DMFs at maintained or better electrochemical protection property offers the replacement of zinc dust layers by technically more powerful zinc flake coatings [8].

In this context, Zinc can be defined as a "super-large-volume-product". In the world, about 10 million tons of zinc are annually processed and more than half of that in the field of rust/steel/building protection. On the other hand, the estimated "loss of steel" by "rusting" is of about 157 Mio tons annually [15].

Zinc-paint, state of the art "commercial" technology and potential
Also in the field of zinc flakes, hereby pigments can be obtained, that are outstanding by easy handling and high corrosion resistance.

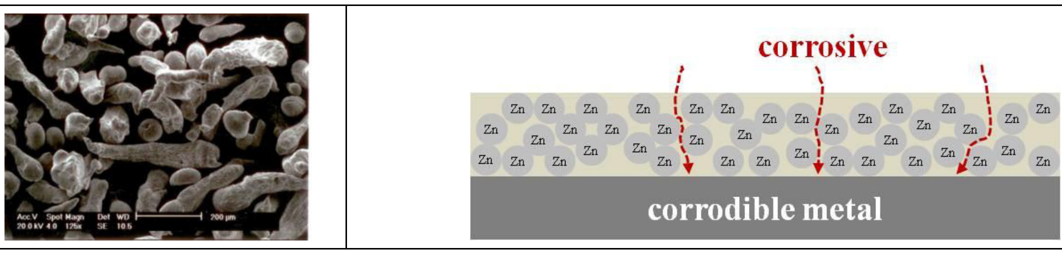

Fig. 2a-b: SEM image Zn-powder and corrosive diffusion, zinc rich coatings with spherical particles

So far known zinc paints with high zinc content are based on spherical or spheroidal particles. The problem of such coatings, however, is the high rate of diffusion of aqueous media by the package-related cavities and consequently, the reduced corrosion protection.

Thin lamellar zinc pigments (ZFP = zinc flake pigments) are mainly used in various applications as anticorrosive pigments in solvent-based paint systems. Due to the dense layer structure, Zinc flake coatings inhibit the diffusion of corrosive media, thus providing a longer protection against corrosion than conventional zinc-rich coatings with spherical particles.

The high kinetic processing (HKP) does not only reduce the zinc particles' size and produces flaky particles, but also increases the level of the stored strain energy accumulated in the microstructure of zinc grains. This stored strain, evaluated from X-ray diffraction analyses, is evident from both the hexagonal lattice distortion and the nanosized conditions of zinc developed after HKP. Moreover, due to the electronegative nature of deformed zinc particles, the thin lamellar microstructure of zinc co-existing with the polymer act as sacrificial anode, thus preserving the integrity of the substrate metal or alloy.

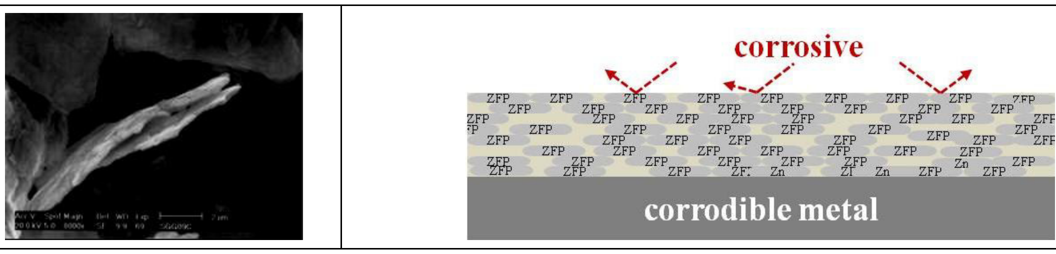

Fig. 3a-b:SEM image HKP-ZFP and lamellar composition of zinc flake coatings

To date, commercially available high-quality zinc-flakes are mainly produced in ball mills using a grinding aid and organic solvents. The production by this method is a highly time and energy consuming procedure, which means by the use of solvents also increases the amount of VOC (VOC = Volatile Organic Compound = volatile organic compounds) and on long term constitutes an environmental risk. Applying organic solvents has hitherto industrially been unavoidable since a wet grinding in aqueous suspension prevents the production of stable flakes. It can therefore not be used in aqueous media.

Innovation & performance

So far commercial available high-quality zinc flakes are mainly offered by a swiss manufacturer who is global market-leading.

By application of HKP it is on the one hand possible to produce zinc flakes effectively and on the other hand possible to obtain combined ZFP compounds by addition of polymer additives as process controlling and dispersing agents. Therefore it is a flexible and economic process. Thus the anticorrosive properties of the ZFP are supported and their stability in aqueous media is improved. Due to the enormous application of energy by the Simoloyer® substantial shorter processing times and a better dispersion and stabilization of the synthesized ZFP are resulting. Thereby a considerable reduction of VOC-containing additives during the process, as known especially from the competitive process technologies, can be achieved. Furthermore the Simoloyer® can be free scaled up to 900 liters process volume, whereby the biggest type of plant - depending on the material - can produce up to 1000 tonnes of nanostructured material. Hence it seems appropriate to work intensively on optimized ZFP by application of HKP and therefore to set the procedural focus on this.

The Simoloyer® technology offers a wide range of procedural possibilities, because there is a rotary born processing system.

Spherical or spheroid Zn- particles are reformed and coated with certain additives in one process step, here the choice of additives is decisive for the later application in the coating system. The manufacturing process of HKP-ZFP has been developed on laboratory scale and has been upscaled successfully to technical and semi-industrial scale. Thereby pigments are formed and coated in a batch process with a volume of 100 liters.

		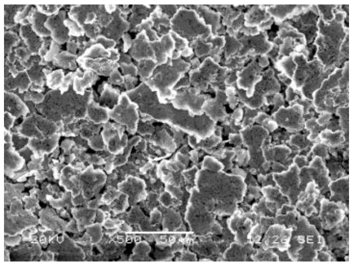
a) charging the Simoloyer® CM100a	b) HKP-plant (Simoloyer® CM100a)	c) HKP-ZFP [1]

Fig. 4a-c: Manufacturing of HKP-ZFP on technical scale by high kinetic processing device Simoloyer® CM100a (Zoz GmbH assembles such devices up to 9x bigger)

Stir-in-pigments

The dispersion of ZFP into the coating system is a problem in solvent-based and even more in aqueous coatings. There is high shear energy necessary to desagglomerate ZFP and disperse them in a certain system. This is caused by the high specific surface and the structure of the Zn-flakes. Suitable dispersing aggregates such as dissolvers, high speed stirrers or similar are not common within trade and not available for the DIY-sector. Manufacturers of coatings offer formulations with colored pigments where colored lacquers can be obtained on site by stirring in pigments in appropriate colored or colorless coating systems. These so-called “stir-in-pigments” are pigments which are covered during production with certain polymer additives that cause the pigments’ agglomerates while stirring to desagglomerate and to generate the desired coloring of the lacquer. Thus a complex dispersing technique of color matching for coatings is not necessary. This concept is realized in HKP-ZFP. These achieve an increased dispersion and storage stability in solvent-based and water-based lacquer systems. Because auf this dispersion of ZFP applying a normal stirrer or some other common mixer in a complete composed corrosion protection coating is possible. This kind of dispersion of ZFP extends the storage durability of aqueous ZFP-lacquer systems, decreases VOC-Emission by use of aqueous corrosion protection systems and develops new application areas for ZFP, which are highly effective for corrosion protection (trade, e.g.).

The so-composed lacquer system consists finally of two components, a complete water-based corrosion protection coating and the ZFP, which are stirred into the aqueous primer shortly before application. With this method the formation of gaseous hydrogen is prevented, like it happens relatively fast during the storage of water-based lacquer systems including ZFP.

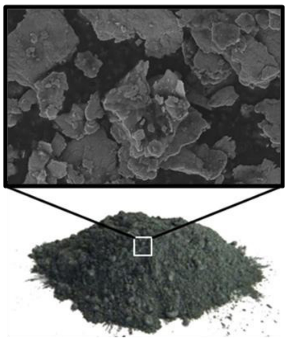		
a) HKP-ZFP: stir-in pigment	b) manual dispersion of HKP-ZFP	c) product: Zoz zinc flake lacquer ZN-CP301

Fig. 5a-c: HKP-ZFP: easy stir- in of pigments without special mixing aggregates

Corrosion resistance
HKP-ZFP have been tested in an epoxy-resin primer.

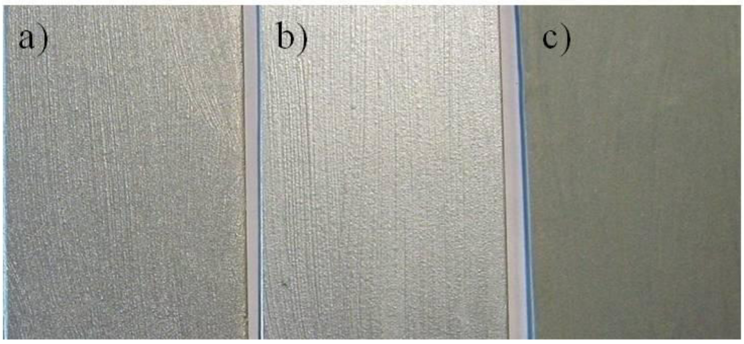

Fig. 6: Coated metal plates with different Zn-primers: a) conventional ZFP-coating, b) HKP-ZFP coating (ZN-CP301) and c) conventional zinc rich coating

In the salt spray test (ISO 7253) as well as in the climatic change test (ISO 6270) coating with HKP-ZFP outmatches coating with common Zn-phosphate pigments. With blistering tests (ISO 4628-2) no blisters appear after 720 h testing, neither within the salt spray test nor within the climatic change test on the metal plates with HKP-ZFP coating. On the opposite the reference Zn-phosphate pigment coating shows after 48 h during the salt spray test and after 240 h during the climate change blisters.

The rust grade (ISO 4628-3) stagnates at Ri 0 with HKP-ZFP containing coatings up to 720 h load period with the climatic change test and 480 h with the salt spray test. According to that HKP-ZFP coatings are suitable for a long protection period (> 15 years) and a corrosiveness category C3. The results of the climate change test even meet the requirements of a long protection period at a corrosiveness category C4. Determination of adhesiveness by ISO 4624 has still to be performed.

Altogether the tested coating including HKP-ZFP meets the demands of the DIY-sector very well.

Further tests in comparison to conventional ZFP-coatings led to similar results.

coating   After salt spray test

a) ZN-CP301

coating   After salt spray test

b) conventional ZFP-coating

Fig. 7a-b: product comparison after salt spray test

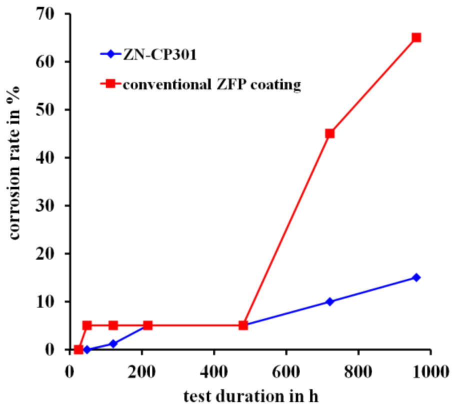

Fig. 8: corrosion rate at salt spray test of conventional ZFP-coatings and ZN-CP301

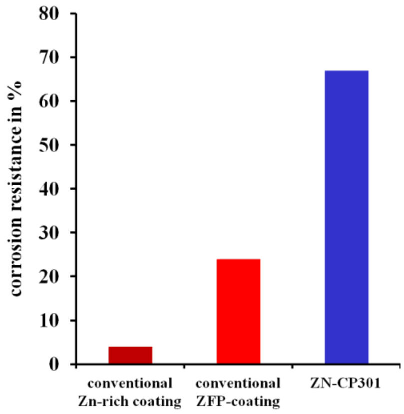

Fig. 9: corrosion resistance of conventional Zn-coatings and ZN-CP301

Water-dispersible lacquers

Zinc shows high reactivity in water-based lacquer systems wherefore just aqueous systems with comparatively low storage stability of few weeks to days are producible yet. In hydrous systems amines are applied as neutralizers. The pigments in the lacquer tend to react in hours to days with water or the amines and to form hydrogen. This causes the low storage stability.

The low storage stability of water-based corrosion protection coatings and coating systems impedes the application in the Do-It-Yourself sector (DIY-sector). A solution is given by the use of corrosion protection system based on two components (2K). The separated storage of ZFP and aqueous coating systems up to the point of mixing and application is very good possibility to increase storage stability of ZFP-based corrosion protection systems considerably.

By its composition the lacquer systems contributes to a sustainable environmental protection. The higher storage stability provides the possibility of a long-term stockpiling. Waste can be saved as no “gassing” overlay old lacquers have to been disposed and the amount of transports can be reduced, which leads to a lower CO_2-emission and reduces costs.

The choice of additive also plays an important role due to the later application in lacquer systems. Fatty acids and fatty acids derivatives are already time-tested. In this case there is a differentiation between leafing- and non-leafing types [9],[10].

Leafing-types create excellent metallic shiny surfaces caused by superficial leafing of the flakes but mostly they are not abrasion- and scratch- resistant. In non-leafing types the zinc flakes are completely dispersed and therefore provide a scratch-resistant corrosion protection. But this causes the color of the system to have a greyish tone instead of a metallic gloss. Because of this additives for the coverage of ZFP have to be chosen according to the basis of the coating, as far as pigments in water-based systems behave vice versa the solvent-based systems.

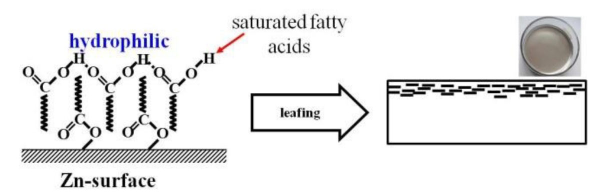

Fig. 10: Leafing-system in a solvent-based lacquer (water-based vice versa) [11]

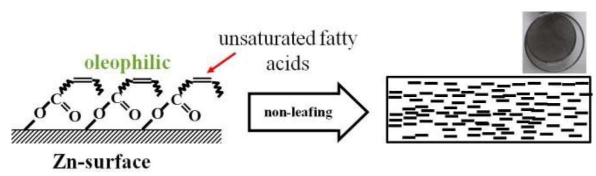

Fig. 11: Non-Leafing-system in a solvent-based lacquer (water-based vice versa) [11]

Tests of the manufactured HKP-ZFP have already been performed in epoxy-resin-based systems as well as in water-based acrylate-systems. According to the choice of additives ZFP show a lower gassing behavior.

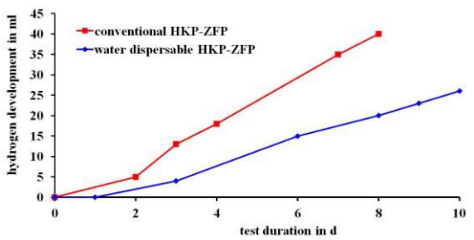

Fig. 12: gassing behavior of conventional coated HKP-ZFP and water-dispersable HKP-ZFP

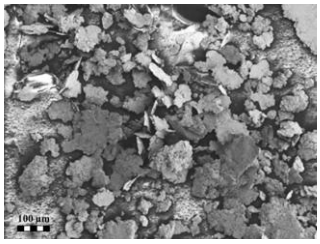

Fig. 13: conventional coated HKP-ZFP

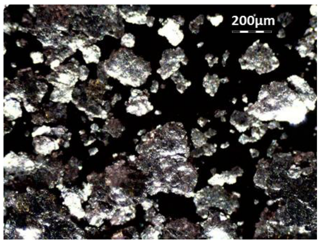

Fig. 14: especially water-dispersable coated HKP-ZFP

According to that the dry coating of HKP-ZFP with certain additives lead to a higher stability in aqueous media which enables a future application of HKP-ZFP in hydrous lacquers with saving of VOC, solvents, transports and process costs at the same time. A small side-effect is the decreased demand on storage space, because fewer amounts of raw materials and process additives, respectively, can be reduced radically. This avoids extensive storage and following storage costs.

Emission saving in numbers and the need for ZFP-coatings

ZFP-coatings are free from chromium and meet without exception the RoHS- and EU- Directives on end-of-life vehicles. Field of application is mainly fasteners für high strength construction parts of the automotive and the building industry. The coating technology is suitable for high quality corrosion protection on undercarriage and structural parts. This increased corrosion protection allows thin walled constructions and leads to further saving of weight and CO_2. Thus a company coats for example engine bearers for the new Mercedes-Benz E-class in a new plant with Zink flake coatings. *By this technique the service provider polishes his car type*'s CO_2-balance sheet: just because of the lower layer weight by 50% of previous coatings the fuel consumption decreases and resulting the CO_2-emission of all vehicles of this type by 352 tonnes per year. Comparable construction parts from Aluminum would cause 37,000 tonnes CO_2-emission additionally during its manufacturing. Accordingly the intelligent use of steel in combination with zinc flake coatings lead to CO_2-*emissions'* reduction during manufacturing and use. [12]

Zinc flake coatings are also used as corrosion protection to the Eurotunnel. This is a further hint on the high performance properties of ZFP coatings. Here the ground soil is wet and the rails of the Eurostar are higher exposed to aggressive media. Therefore ZFP coatings are a utilized. [13]

Costs according to corrosion damages have been about 3.3 billion (10^{12}) US$/a, which is over 4% of the global gross domestic product [14]. They originate from maintenance, protective precautions, replacement of corroded parts and breakdowns because of corrosion. Globally 5 tonnes steel per second are destroyed by corrosion. [15]. Healthy risks due to emitted heavy metal particles are a not negligible fact, as well as safety risks by destroyed or damaged parts.

Realization & Planning

Further development of HKP-ZFP to stable water-dispersible pigments and lacquer system based on them is a continuing process and will be still followed up in future. Previous results are promising and will break a path to a future with water-based economical and ecological efficient high performance stir-in lacquers for industrial, trade and Do-It-Yourself utilization.

What we offer

Zoz is neither pigment nor lacquer manufacturer and shall, can and will also not become so. All the above activities are aimed explicitly to the goal to be able to provide the appropriate technology. On the way to there it is certainly possible to offer - and so already practiced - small amounts of HKP-ZFP and ZN-CP301 e.g. up to 6 kg.

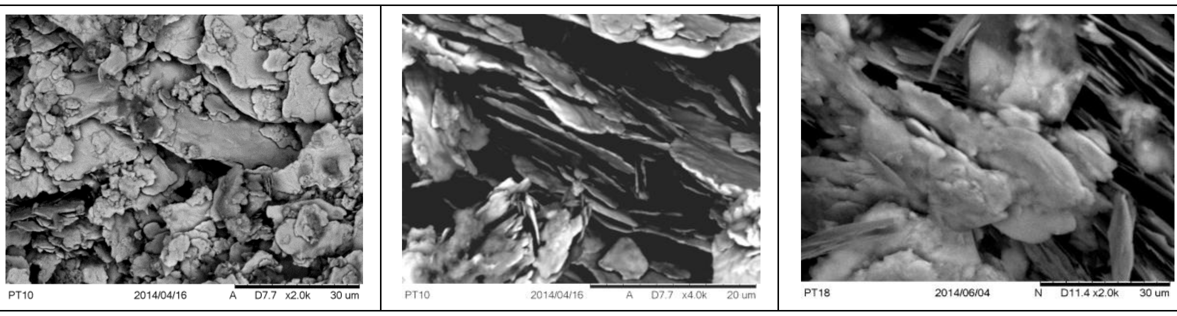

Fig. 15a-c: Different Additives, different morphologies of ZFP

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