Emulsified Nutritive Fluids and Their Properties Control

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A new approach of the foliar nutritive fluids formulation as emulsions and their properties design was grounded on the last illuminations in the mechanism and kinetics of the foliar nutrition. Emulsified organic and inorganic phases are bearing extended multifunctional biological activities – nutrition, growth enhancing and fungi repelling. Selection of the overbasic potassium salts of naphthenic and oleic acids as organic phase carrier entrusted leverage control of the foliar required properties through their overbasicity, hydrolysis and hydrolysis pH, as well as through the mixed organic/inorganic hydrolysates particle size distribution inside the film formed at the foliage surface. Aqueous phase may accommodate variable formula of NPK macronutrients and regular contents of micronutrients under suited restrictions called by the emulsion stability. Due to the both phases reactivity, at the foliage level the diluted fluid leaves a matrix made up by organic hydrolysates, grafting the entire mineral charge as an amorphous phase ready to dissolve at high rate. All new born biological active entities are released by organic matrix as nanoparticulate amorphous matter, as well as micelles charged with amorphous nanoparticulate at a rate close to plant demands, preventing overdosing and eventual plant harms. All nutritive fluid components are biodegradable or non harmful for environment. The sorption mechanism-property correlations are illustrated by property-composition diagrams, pH monitoring during organic matrix precipitation and reaction with air carbon dioxide, dynamic particle size distribution in hydrolyzing emulsions, and film morphology in correlation with nutrients concentration distribution in layered film.

Keywords: foliar, nutrition, growth enhancing, fungicide

Extensive use of foliar products as complementary nutrient sources and growth enhancers or pesticides is beyond any doubts one of the most simple and efficient ways to handle crop control during any vegetative development stage. Nevertheless, the refining quality of foliar products, even for small adjustments in composition for balancing plant transient demands, is confined to restrictive limits due to objectionable changes in the physical properties required for foliar application, as: complete solubility, uniform distribution on foliage, adherence, hiding power, penetration power through waxy cuticles, cell walls and plasma cell membrane, low saline and contact stress or environmental friendliness, etc. A short review over the above properties might show that a great deal of them could hardly be associated with saline solutions of nutritive elements compounds or with mixtures of growth control organic substances. Our previous works in the field of formulation emulsified nutritive fluids were mostly focusing on the empirical ways to accommodate organic components into usual NPK foliar fertilizers for better control of their foliar properties, as well as for grafting them additional growth enhancing and fungicide functions [1-8].

This paper brings about a new approach of the subject taking the foliar penetration mechanism and its kinetics as a keystone in formulating and product properties modelling. According to this concept these foliar fluids have to be concentrated emulsions containing two distinctive phases: an organic phase which is the carrier, providing additionally growth enhancers and fungicides beside carbon dioxide reactive components able to hydrolyze over foliage surface, and an aqueous carried phase yielding all the mineral constituents of usual NPK liquid/foliar fertilizers with or without micronutrients at a prerequisite level. After dilution and spreading over the foliage, and subsequent water evaporation, the emulsion leaves at the foliage surface a thin matrix layer incorporating the entire saline/non saline mass from aqueous phase as a new born mixture of amorphous or micellar nutritive species.

Original approach of the hydrolyzing emulsion application and leaf born nutritive species was fulfilled with high regard to the permeation of the biological active entities through cuticle by both lipophilic and polar paths of diffusion. Consequently, the emulsion components selection has been made in good agreement with the mass transport mechanism of lipophilic species through cutin wax domains [9] as well as with high humidity/hydrolysis promotion at leaf surface in order to activate the cuticular permeability to water and non lipophilic species [10]. Reliable correlations composition-property were searched for finding adequate balances in chemical formulation and foliar products required properties.

Materials and methods

Reagents, Additives and Bulk Chemicals

Naphthenic acid (purified molar mass 190) SC Sotech SA Romania; Naphthenic acid (refinery crude grade molar mass 311 and purified molar mass 275) SC Petrobrazi SA Romania; Oleic acid (98% p.a. molar mass 282) Fluka GmbH Germany; Oleic acid (technical grade molar mass 282) SC Sin SA Romania; Potassium hydroxide (85 and 98% p.a. pellets) SC Chemapol SA Czech Republic; Potassium hydroxide 40%, electrolytic solution p.a. SC Chimopar SA Romania; Potassium carbonate and potassium bicarbonate SC Chimopar SA Romania; Calcium and magnesium salts p.a. SC Chimopar SA Romania; Ethanol 96% p.a. SC Chimopar SA Romania. All the products

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entering into each considered formulation are not toxic and biodegradable [11-15].

Synthesis Protocols and Experimental Developments

Overbasicity of the metallic salts of organic acids is defined as molar ratio between metallic oxides and correspondent acids. Most of such salts are water insoluble products, excepting the alkali metal and ammonium compounds. This class of products gather many distinguished physical properties from which their capacity to pass into stable aqueous emulsion may be exploited in order to prepare dispensable liquid products. Other emulsion properties (*p*H, viscosity, surface tension, stability etc.) may be easily adjusted by addition of new components. All overbasic salt emulsions are easily hydrolyzing, when are diluted with water. Protocols set upon for solid-liquid and liquid-liquid phase equilibriums study were used for investigations on pseudoternary systems overbasic naphthenate/oleate-water-ethanol isotherms and properties [16]. Some accurate weighted mixtures of water potassium hydroxide and naphthenic or oleic acid with the same molar ratio $K_xR(OH)_{x-1}$ (overbasic salts were considered unitary components), under constant temperature (30°C) and continuous stirring, were slowly titrated with ethanol until the entire mass of solid phases was totally passed into a clear emulsified phase. For reliable drawing of the curves separating stable emulsion domain from polyphasic domain, the choice of particular ratios $H_2O/K_xR(OH)_{x-1}$ covered the entire aria of ternary compositions (fig. 1). Density, surface tension, viscosity and other properties related to foliar layout along boundary of clear emulsions in figure 1, were measured by usual standard procedures and specifications. Carefully selected emulsion formulae were used to demonstrate the overbasic salts functionality as intermediary products in advanced foliar nutritive fluids properties design. Some simple laboratory experiments provided data on hydrolysis and *p*H control, hydrolysate structure and layering, reactivity of the applied emulsion and its compatibility with hard waters. Layered applied hydrolyzing emulsion behavior and properties have illuminated the assumed mechanism of foliar absorption.

Crystal size analysis and sprayed pellicular film morphology

Crystal size distribution in diluted emulsions was measured with a Zetasizer nano instrument ZEN 3600. SEM microscopy coupled with EDX spectroscopy System VEGA II LMU was used for pellicular film morphology investigation and elemental analysis in the dried pellicular films.

Results and discussions

Composition – Property Diagrams

From engineering point of view the plant cuticle is a roughly textured uneven mobility/solubility membrane. Its permeability to non-ionic organic substances is imparted by two parameters: lipophilicity and mobility. Lipophilicity is related to the non-ionic organic compounds solubility into the mass transport limiting layer. Mobility accounts for the diffusion of lipophylic compounds across the mass transfer limiting layer on waxy cuticle surface. Both parameters strongly depend on the size of diffusing organic molecules, as well as on the fluid viscosity and surface tension [9,17]. According to the presumed acting mechanism of the new emulsified foliar nutritive fluids, the selection of lipophilic organic carrier phase or lipophilic species of growth enhancers and fungicide has to put forward as a critical criterion the low molecular mass for at least main components.

Overbasic potassium salts of the naphthenic and oleic acids, picked up as intermediaries bearing the physical and chemical properties matching the above selection criterion, are non-crystalline materials with poor solubility in water. Meaningful overbasicity and additives choice may produce aqueous emulsions/solutions of these salts bearing mandatory properties for foliar applied fluids. Moreover, both naphthenic and oleic acids themselves are carrying growth enhancing [18,19] and respectively fungicide properties [20]. On the other hand, the use of ethanol as the third component in the pseudoternary system overbasic salts of the naphthenic and oleic acids-water-ethanol is a good replacement for the random and mostly insecure choice of other compatibility additives, because the miscibility water- ethanol and ethanol-organic acids provides a convenient weight in handling the mixture properties and shifting them to worthwhile values. Thus, the pseudoternary systems overbasic naphthenate/oleate-water-ethanol isotherms subsuming overbasicities from 2/1 to 6/1 were investigated at 30°C (fig. 1). These diagrams provide valuable information about the balanced compositions which may carry demanded properties in both concentrated emulsified fluid and diluted hydrolyzing solutions. Boundary between liquid phase surface (stable clear emulsions or solutions) and solid/liquid phase mixtures surface is the pseudo-equilibrium curve interconnecting the solubility points of overbasic salt in water, and respectively in ethanol. Shape of this curve is the result of chemical interaction between potassium hydroxide and ethanol. On the left side, when ethanol was

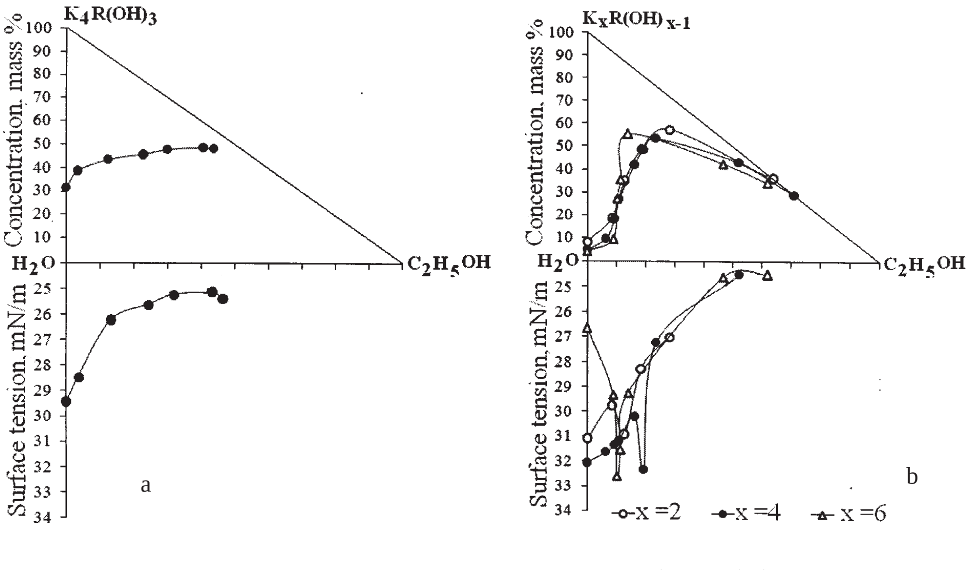


Fig. 1. Pseudo ternary systems overbasic potassium naphthenate – water – ethanol (a) and overbasic potassium oleate – water – ethanol (b) at 30°C; Overbasicity 2/1, 4/1 and 6/1; Composition – surface tension diagrams

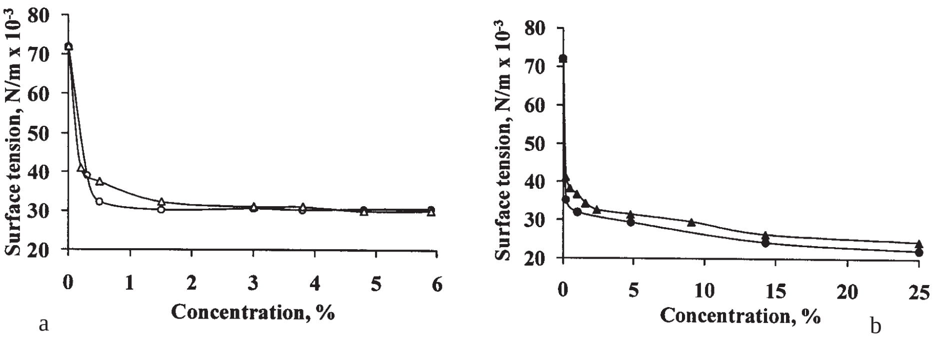


Fig. 2. Surface tension versus the concentration of 4/1 overbasic salt emulsion diluted with deionized water. Potassium oleate 4/1 non pre-carbonatate (O); Potassium oleate 4/1 pre-carbonatate (●); Potassium naphthenate 4/1 non pre-carbonatate (Δ); Potassium naphthenate 4/1 pre-carbonatate (▲)

added to aqueous solutions of overbasic salts the following reaction takes place:

$$C_2H_5OH+KOH \leftrightarrow C_2H_5OK+H_2O \qquad (1)$$

As far as potassium hydroxide is consumed, the overbasic salt apparent solubility increases and reaches a maximum, while the reaction (1) attains equilibrium. New ethanol adding brings about salting out and hydrolysis of the overbasic salts and, consequently, a huge decrease in overbasic salts solubility. The IR data on solid and liquid phases separated on the right side of equilibrium curve backed up these assumptions. Our previous empirical findings on pseudo-binary systems overbasic naphthenate/ oleate- water were concluded with the assessment of the 4/1 overbasicity in terms of molar ratio KOH/fatty acid and a total concentration of 1 mol/L in terms of potassium hydroxide as appropriate composition bearing the foliar emulsion intermediaries best properties as density, surface tension and viscosity [3]. Composition-property diagrams like these from figures 1 yield new data and leverage prospects due to ethanol share in properties adjustment and control. Beside, small ethanol concentrations in both concentrated emulsions and diluted spraying solutions certainly remove chemical destabilization of the emulsion and may amend positively the density, surface tension and viscosity. On the other hand, moderate diminution in density, viscosity and surface tension achieved by ethanol improves the mobility of lipophilic species (naphthenic and oleic acids) through liphophilic domains in waxy cuticle and brings about higher penetration rates through cuticle polar pathways for all species born in hydrolyzing diluted fluids. Figure 2 shows the variation of emulsified nutritive fluids surface tension on dilution to appropriate concentrations for use as foliar spray. Both intermediary display low surface tensions, ranging below 40 mN/m, for any concentration less than usually recommended 1% (grams of concentrated emulsion /100 g of solution). As far as the fluid pre-carbonation process, accepted as a mean to reduce pH of the applied product, do not alter significantly the diluted solution surface tension, it is expected that other component (containing nitrogen, phosphorus and potassium) or hard water used for dilution will not change to large extent solution/emulsion surface tension. Some other properties linked to fluids foliar application may be disclosed by similar composition-properties diagrams as those presented in figure 1.

Particle size distribution dynamics

Potassium overbasic naphthenates hydrolysis, and further carbonation and water evaporation are discharging on the foliage film precipitated solid phase of all organic and inorganic hydrolysates. Firstly, on dilution particle size distribution are generated only the organic components, mainly potassium overbasic naphthenates and oleates. Some stability in this particle size distribution is highly required during the spreading and film formation. If the size of the newly born hydrolysates ranges around some hundreds of nanometers full spreading and equal distribution of the fluid and its components on the foliage might be easily reached. Particle size distribution was measured over 40 min interval since the potassium

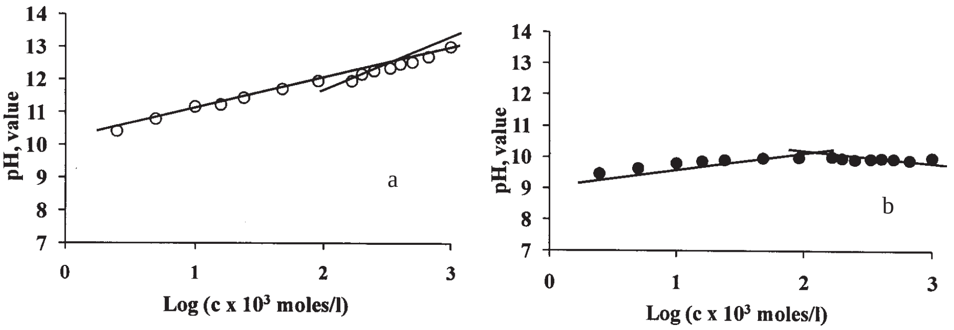


Fig. 3. Hydrolysis of potassium overbasic naphthenate (4/1) 1M(K) non pre-carbonated (a) and pre-carbonated up to *p*H 10 (b) during dilution with deionized water

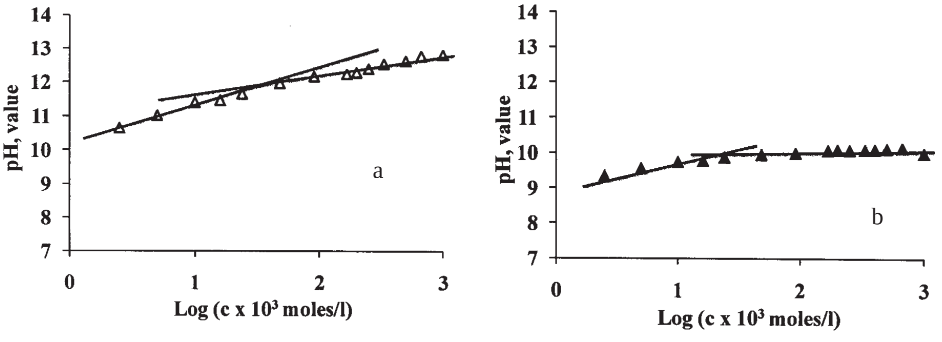


Fig. 4. Hydrolysis of potassium overbasic oleate (4/1) 1M(K) non pre-carbonated (a) and pre-carbonated up to *p*H 10 (b) during dilution with deionized water

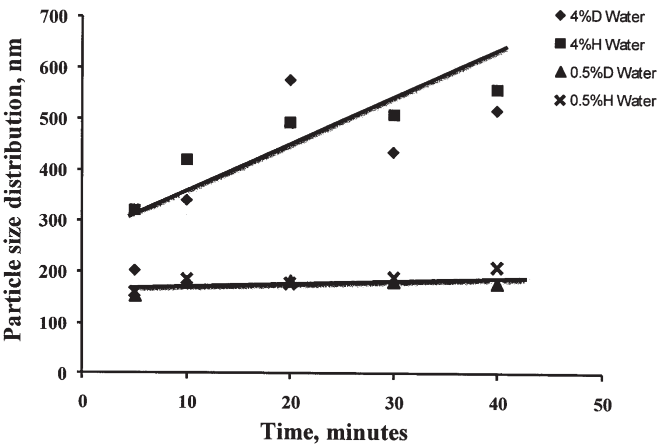


Fig. 5. Particle size distribution in potassium overbasic naphthenate emulsion

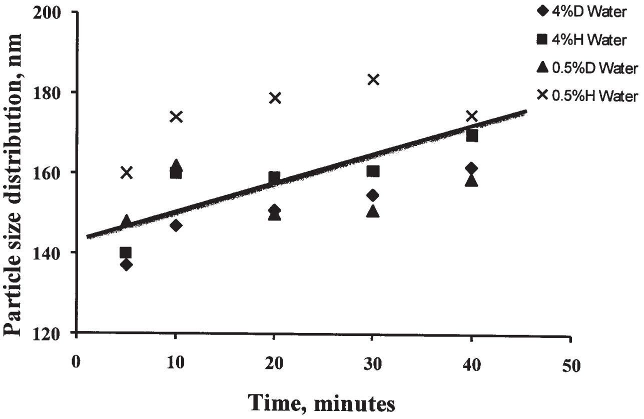


Fig. 6. Particle size distribution in potassium overbasic oleate emulsion

overbasic naphthenate (overbasicity 4/1 and concentration 1M) and potassium overbasic oleate (overbasicity 4/1 and concentration 1M) respectively, were diluted with demineralized and hard water (60 mg/L). The results of these measurements are given in the figure 5. Both product hydrolysis exhibits quick and complete reactions which went on with the formation of stable low size particles. For potassium overbasic naphthenate hydrolisates the particle sizes are ranging between 200-500 nm in 4% diluted emulsions and between 15-200 nm in 0.5% diluted emulsions (fig. 5). Unexpectedly, hard water does not change significantly the particle size distribution (fig. 5). Accordingly, we conclude the calcium from hard water interacts with naphthenate ion, but in the limits of calcium naphtenate solubility at the dilution water temperature. Moreover, on short interval of time, without substantial carbonation and water evaporation, some other particles do not nucleate, and older particles do not grow and do not associate in larger clusters. In similar way proceeds the hydrolysis and particle nucleation in potassium overbasic naphthenate (fig. 6). Particularly, in this case, dilution and hard water do not modify the range of particle size distribution, which is laying in the range 100-200 nm (fig. 6). The determinant force in control particle nucleation process and its consequence - uniformity of particle size distribution occurrence in diluted emulsions- is undoubtedly low surface tension in aqueous media and capacity of both overbasic salts to form stable emulsions. When carbonation advances and small quantities of the water in hydrolyzed film were already evaporated, the emulsion is breaking and particles may grow or agglomerate to higher dimensions. These processes outcome was visualized in microscopic analysis of the samples layered on under different conditions for some more intermediary products containing potassium overbasic naphthenate.

Intermediaries Hydrolysis

Hydrolysis of the overbasic salts of fatty acids from diluted emulsions is a well known process, occurring due to poor strength and low solubility of the organic acids in water. But, this property was never used neither for shaping a way for foliage layer precipitation or matching layer properties to the mechanism of foliar absorption, nor for the precipitation of new born growth stimulating species inside the hydrolysate layer. However, our initial assumptions on hydrolysis process originate from the workable step by step reaction of carbonation with free air carbon dioxide, able to push the *p*H beyond a certain hydrolyzing point and help adherent layers precipitation, while other species of nutritive compounds are nucleated from diluted emulsion over hydrolyzing mass and grew as amorphous or poor crystallized phases. The figures 3a and 4a illustrate the hydrolysis onset process going on at a *p*H dependent on dilution ratio of the overbasic naphthenate (molar ratio 4/1 and 1M), respectively potassium overbasic oleate (molar ratio 4/1 and 1M) emulsions. The slope break on *p*H versus dilution ratio plot assigns the hydrolysis onset point to *p*H 11.5 for potassium overbasic naphthenate, respectively to *p*H 12.2 for potassium overbasic oleate. These unreasonable pH values must be cut down to less than 10.00 to ease the stress or burn of plant foliage. Most simple way to do this is to carbonate concentrated emulsions down to *p*H 10.0 or to alter its composition replacing parts of potassium hydroxide with equivalent parts of potassium carbonate or bicarbonate outside the range of emulsion destabilization. Figures 3b and 4b display the outcome of proper preliminary overbasic salts pre-carbonation, when hydrolysis onset is brought down to pH 9.7-9.9 close to a fatty acids concentration of 1.5-2.0 x10^{-3} mol/L. Further ease in *p*H foliage stress can be conveyed by hard waters use for dilution. In this case the hydrolysis onset is triggered by calcium and magnesium fatty acid salts nucleation. Some other parameters may also shift the hydrolysis point in a convenient *p*H domain. Nevertheless, working on overbasicity, carbonation degree and ethanol concentration seems to be a fair reasonable way for control diluted spraying fluid *p*H. Since the overbasicity was framed to 4/1 by other physical properties assessment (density, viscosity, surface tension), only the pre-carbonation, dilution and component ratios in concentrated emulsion may force the hydrolysis outburst immediately after the application.

Hydrolysate Layer Precipitation

Taking advantage of the easy way to measure the thinly layers *p*H with dry sensors, the hydrolysate layer precipitation process was monitored through pH measurements over the entire duration of applied liquid layer carbonation process accompanied by a partial water evaporation. Actually, a drop of freshly diluted sample of each intermediary (concentrated emulsion of the overbasic 4/1 potassium oleate and respectively naphthenate) was left to dry off on the surface of pH-meter dry sensor, measuring continuously the pH variation. We assume that immediately after application the emulsified overbasic salts hydrolysis advances due to air free carbon dioxide absorption and the liquid film breaks out in a discontinuous micelle structured fluid leaving on the leaf surface an adherent layer of organic hydrolysates. The micelles have a core of free organic acids covered by a highly hydrated

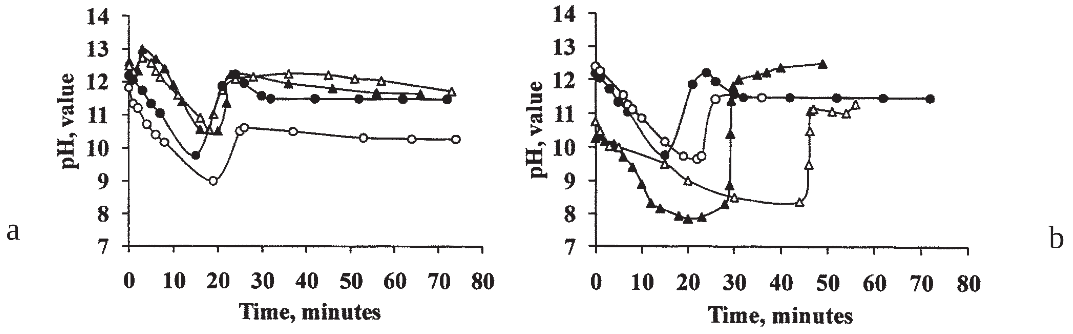


Fig. 7. a) Layered matrix precipitation in non pre-carbonatated naphthenate $K_4R(OH)_3$ 1M. Diluted solutions 1/25 (▲), 1/50 (Δ), 1/100 (·), 1/200 (o); b) Layered matrix precipitation in non pre-carbonatated $K_4R(OH)_3$ 1M, diluted 1/100 (•); $K_4R(CO_3)_{3/2}$, diluted 1/100 (▲) 1M; $K_4R(OH)_3$ 1M + urea, diluted 1/100 (o);$K_4R(CO_3)_{3/2}$ 1 M + urea, diluted 1/100 (Δ)

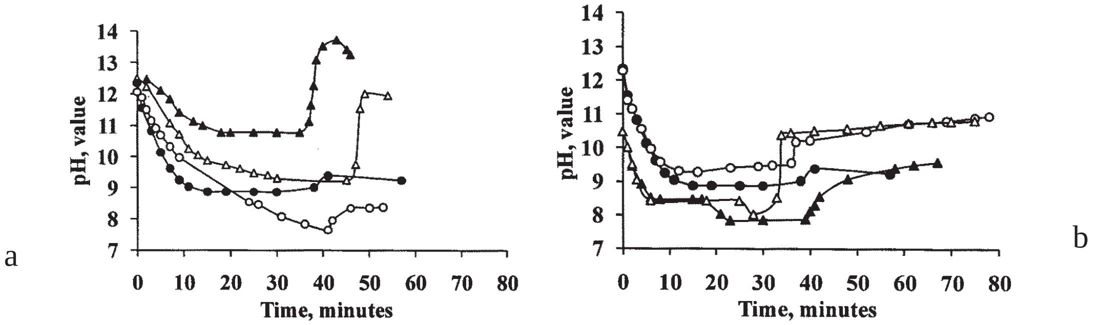


Fig. 8. a) Layered matrix precipitation in non pre-carbonatated oleate $K_4R(OH)_3$ 1M. Diluted solutions 1/25 (▲), 1/50 (Δ), 1/100 (•), 1/200 (o); b) Layered matrix precipitation in non pre-carbonatated $K_4R(OH)_3$ 1M, diluted 1/100 (•); $K_4R(CO_3)_{3/2}$, diluted 1/100 (▲) 1M; $K_4R(OH)_3$ 1M + urea, diluted 1/100 (o);$K_4R(CO_3)_{3/2}$ 1 M + urea, diluted 1/100 (Δ)

shell of metallic carbonates/hydrogen carbonates or hydroxides/carbonates, whose alkalinity is continuously diminishing as far as remaining water is still providing some reactivity for furthermore carbonation. On the other hand, the carbonation process up to higher hydrolysis level promotes inorganic phase nucleation and growth over the hydrolysates layer. While the hydrolysis and carbonation progress in extent, there is expected a significant decline in liquid phase *p*H, because more and more hydroxyl ions are bound into hydrolysate complexes. Minimum value of *p*H is reached when full hydrolysis is achieved and organic layer building up ceased. Further water evaporation may raise eventually the hydroxyl concentration in liquid phase, but this scenario is valid only if the foliar absorption does not take place simultaneously with hydrolysis and carbonation. Our experimental data (fig. 7 and 8) match in depth the above mechanism of organic layer precipitation and minimum descent of *p*H values were clearly recorded. Up to this minimum, the real process on the foliage might follow the same path with adjoining results. Beyond this stage, all the pH measurements are impaired fouling of the dry sensor surface and equally by the raise of organic components in the liquid phase due to advanced water evaporation stage. Nevertheless, the progress in *p*H raise is expected and motivated by solid components outgoing from solution (similar to alkaline solution carbonation up alkali metal hydrogen carbonate precipitation), but certainly on shorter intervals. Hence, the curves from figures 7 and 8 are inaccurate replicas of the hydrolysate layer carbonation and precipitation, mainly from its moment up to full precipitation to late water evaporation stages at the end of experiment. Other way said, the factual behaviour hydrolysate layer matrix is a little different, because the nucleation and growth of layer charges, comprising hydrolisates and inorganic component particles, occur simultaneously with selective foliar absorption of some nutritive and growth enhancing species. Thus, lower raises in pH are expected after the minimum value of *p*H in figures 7 and 8. Other species, like potassium hydrogen carbonate, coming from the final stage of air free carbonation, may subsist for longer time on foliage accomplishing its task as ecological fungicide. Because the micelle film is soluble at a *p*H higher than 8.0, this mechanism of action excluded over dosages and let the leaf to take as much of the nutrients as its capacity to generate alkaline metabolites may yields or daily leaf moistening allows. Due to its composition, the organic film liberates slowly and discontinuously, step by step, all the nutritive, growth enhancers and fungicide entities until the film depletion and final auto-destruction.

Figures 7a and 8a show how dilution may be handled to control not only the onset *p*H of hydrolysate layer nucleation, but also the precipitation rate of both hydrolysate and amorphous/poor crystallized inorganic components. Additional quantities of potassium carbonate to replace potassium hydroxide in overbasic salts, and respectively urea to charge nutritive fluid formula with nitrogen up to a molar ratio N/K 4/1, do not change the hydrolysis mechanism. This only affects the onset hydrolysis *p*H and precipitation rate (figs. 7b and 8b). Higher *p*H values on right side of figures 7 and 8 have to be seen mostly as faulty records of sensors in organic/inorganic saline mass lacking minimal moistening water.

Layered film morphology and nutrients concentration distribution in particulate film

For studying and characterization of the layered emulsions films there were prepared some samples of intermediaries used in the formulation of emulsified

Table 1
INTERMEDIARY PRODUCTS AND FULL FORMULATION OF NUTRINAFT EMULSIFIED NUTRITIVE FLUID

Product	Compozition	Suplementary treatment
Potassium overbasic naphthenate	Naphthenic acid 0.25 M KOH 1M	Carbonated up till pH 10
Potassium overbasic naphthenate containing urea and ethanolamines	Naphthenic acid 0.25 M KOH 1M $CO(NH_2)_2$ 1.5M Ethanolamines 0.1M	Carbonated up till pH 10
Urea and ammonium orthophosphate	$CO(NH_2)_2$ 1,5M NH_3 0.5 M H_3PO_4 0.5 M	KOH added up till pH 10
Nutrinaft	KOH 1M Naphthenic acid 0.25 M $CO(NH_2)_2$ 1.5M Ethanolamines 0.1M H_3PO_4 0.5 M Micronutrients (boron, copper, zinc and molibden), normal rates Additives, normal rates	Carbonated up till pH 10

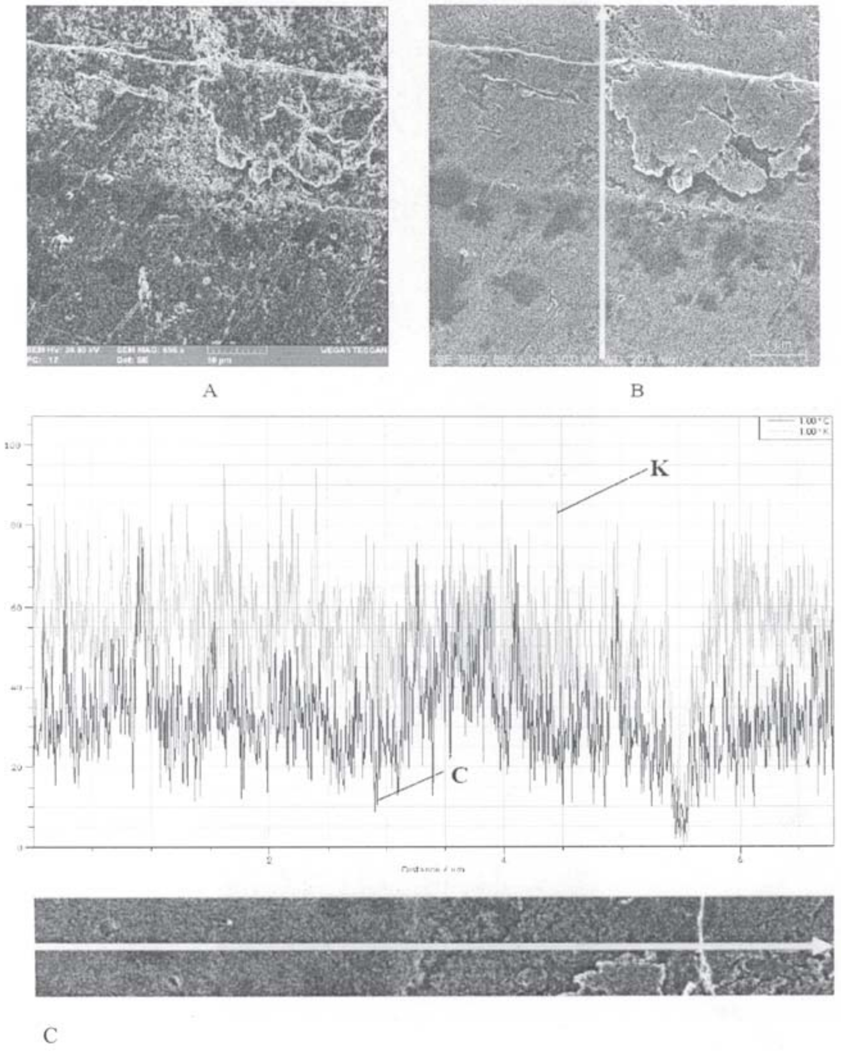


Fig. 9. Potassium overbasic naphthenate cast on nickel substrate. A) Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis

nutritive fluid and a typical foliar applied liquid fertilizer (table 1).

The particulate structure of potassium overbasic naphthenate film deposited on nickel foil placed on microscope holder has at least two overlapped discontinuous layers (fig. 9A). Entire material is amorphous, with some individual particles distinctly broken from the layered structure. Border layer structure can also be seen in the figure 10B, were the film was cast on a glass lamella and dried into the air. Uniform density particles layout is building up the porous layer outface (fig. 10). Individual particles size may be around the same dimensions as the clusters observed in the sprayed diluted emulsion (fig. 5), but due to the partial carbonation they could lay to smaller sizes (fig. 10A). The thickness of the deeper layer is less than 1000 nm. Actually, this is the longest way the microscope detector can find out the nickel structure underneath of the hydrolysate layers (figs. 9B, 9C and 10D). The hydrolysate layers precipitated on both type of substrates in figures 9 and 10 have a very uniform distributed composition. Profiles concentration of carbon (coming from naphthenic acid) and potassium (coming from

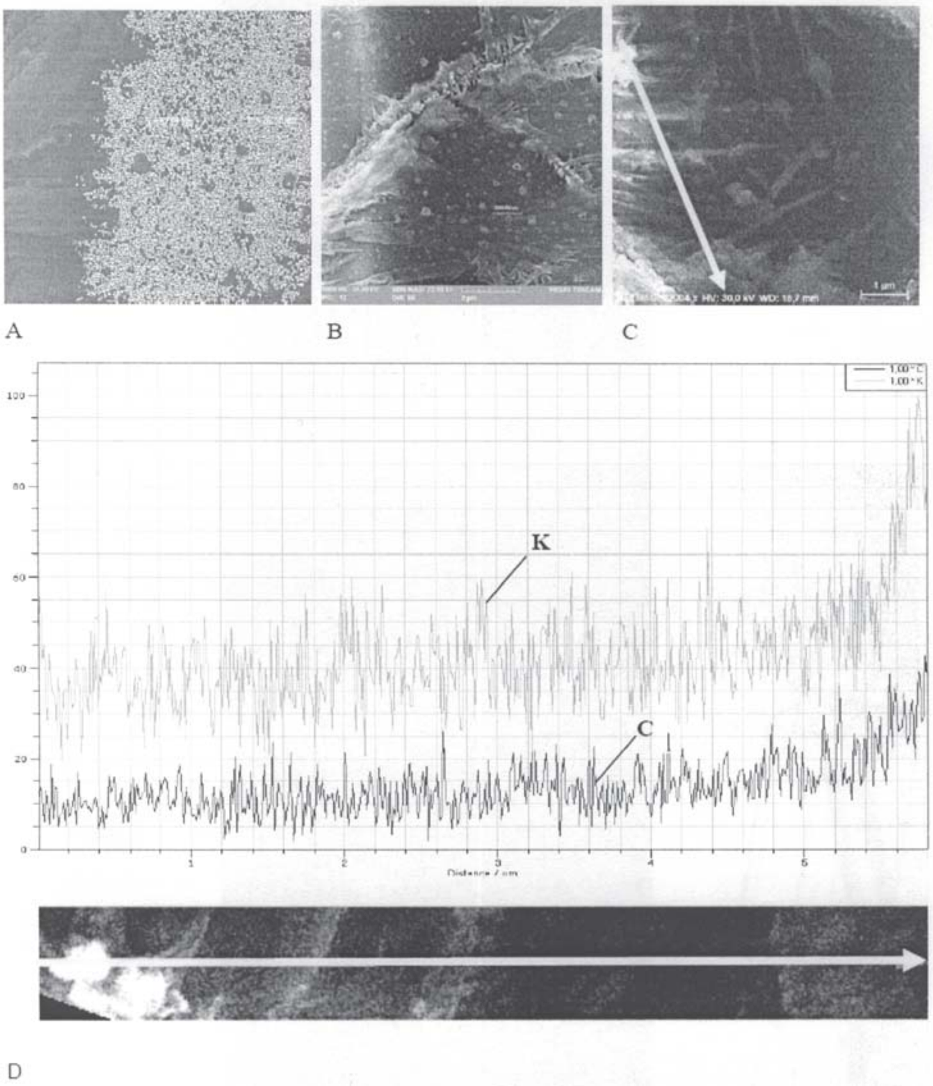


Fig. 10. Potassium overbasic naphthenate cast on glass substrate. A) Film particulate structure; B) Film thickness and elementary analysis profile; c) Reference concentration profile; D) Profile EDX analysis

potassium hydroxide) are given in the figures 9C and 10D. Their particular patterns in both elements concentration bring on the real clues about the uniform distribution of potassium in the mass of naphthenic acid hydrolysates and the variable bonding ratios of the potassium to carbon as naphthenate on hydrolysate surface.

Urea is a good emulsifier in non miscible organic compounds mixtures. It is supposedly expected that urea will stabilize the potassium overbasic naphthenate emulsion and, consequently, it will be the best nitrogen carrier in the emulsified nutritive fluids. Layering ways of the mixtures between urea and potassium overbasic naphthenate are visualized in the figure 11. Two amorphous layers are clearly seen, as well as the gap in the outer side film layer. Both layers contain the two compounds in different ratios. The one deposited right on the substrate contains much more urea and the surface one much more potassium naphthenate hydrolysate. Both layers are mainly amorphous and hydrated, but some individual particles with a poor crystalline structure have been separated over middle gap and on the top layer (figs. 11A and 11B). In the central part of both 11A and 11B figures there is a quite distinctive piece of agglomerated particles of urea imbedded in an over ridged mass of hydrolysated of potassium naphthenate. More plainly information about this structure is rendered out from the figure 11C. The potassium concentration profile drops along the section line; either the carbon concentration profile. Factually, potassium naphthenate hydrolysate concentration is at lower level over the central gap profile, but at quite the same level into the both sides of gap. Thus, the piece of agglomerated particles contains manly urea. Because urea is uniformly distributed over the entire profile, there are many reasons to admit the deeper layer of the film is made up from a mixture of predominantly urea and naphthenate hydrolysates. The upper layer covers only the central gap and contains also a mixture of predominantly potassium naphthenate hydrolysate and urea. This insight interpretation is baked up by figure 11D which shows this layer accumulate increased concentrations in potassium and carbon, and rather common nitrogen concentrations as in the deeper layer. The nickel concentration profile confirms the layered pellicle thickness is not higher than 1000 nm as it was mentioned above.

Figure 12 describes very well not only the layered structure of dried material, when the full emulsified nutritive fluid is applied on a solid material surface, but the interesting evidence about the kinetics of pellicular film formation. When the diluted emulsion was spread on the nickel substrate for analysis, a film of poorly hydrolysed product covers a delimited area. As far as hydrolysis advances, more hydrolysed naphthenic acid is emerging at the substrate surface carrying with it large quantities of hydration water, whose main component is urea. During the further pellicle carbonation and drying the wet area is contracting and braking into little islands on the top of the hydrolysed layer. Finally, the inorganic compounds and urea begin to precipitate mainly as highly hydrated amorphous solid phases. At the end of drying process the sprayed area is covered with a deeper layer containing chiefly the mixture

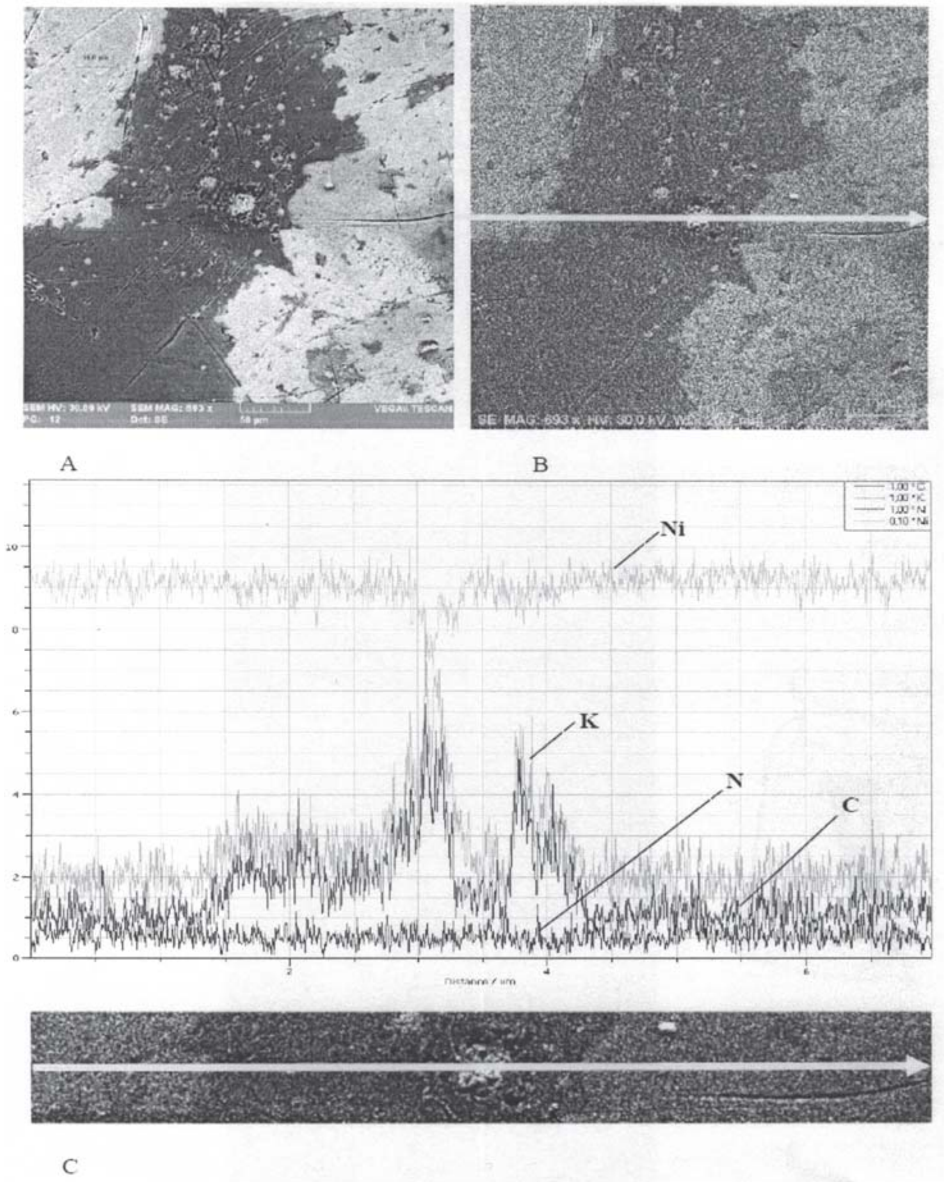


Fig. 11. Potassium overbasic naphthenate mixture with urea cast on nickel substrate. A) Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis

urea-potassium naphthenate hydrolysates. On the top of this layer there are some other fragmented layers incorporating foremost of the inorganic species from the initial diluted emulsion. All these facts are obviously seen on the figures 12A and 12B. More knowledge about the distribution of chemical species between the overlapping layers can be concluded from figure 12C. The EDX profile of concentrations shows some accumulations of potassium and phosphorus inside the top isolated islands; hence, the mono and dipotassium hydrogen orthophosphate outcome as main components of the top layer. Smaller leaps of carbon concentration from the basis line along the profile concentration inside the islands layered surface certainly accounts for liquid pellicle carbonation and potassium carbonates precipitation together with potassium orthophosphates. Inside deeper layer laying on the substrate surface, the profile concentrations of carbon (accounting for naphthenic acid and urea), nitrogen (accounting for urea) and potassium (accounting potassium overbasic naphthenate) stand for the homogenous distributed mixture between urea and potassium naphthenate hydrolysates. The figure 13 corroborates the data about potassium hydrogen orthophosphates precipitation on the top of lower layer of urea and potassium naphthenate hydrolysate mixtures. Apparently, the crystallite branch shaping suggests some earlier form of crystallization, but the material is in an amorphous particulate state with acicular units of hundreds nm dimension. Also, the figure13C confirms the exclusive presence of potassium and phosphorus in the top broken layer as mono and dipotasium hydrogen phosphate. Actually, exceeding potassium in potassium overbasic naphthenate and five time lower phosphorus concentration highlights the prevalence of the $H_2PO_4^{-1}$ ion at the expense of HPO_4^{-2}.

The nutrients distribution on the layered surface particular point is envisaged on the microphotographs and table from the figure 14. The analyzed microphotoggrph is most complex one because the Nutrinaft products layered film contains the at least one chemical compound for each of the nine basic elements. The analysis points were placed on 2 small islands formed on the broken top layer, one on big island and the last on the first layer precipitated out of a particular mixture of urea and hydrolysed potassium naphthenate. The choice was not achieved randomly. Representative data were selected from a larger number of measurements. The small size islands (upper 2 figures) subsume predominantly potassium and phosphorus accompanied by urea, represented as nitrogen. Most of copper and partially zinc and boron are incorporated may be as phosphates or naphthenates. Larger size island coming from the same top layer seems to bear the same

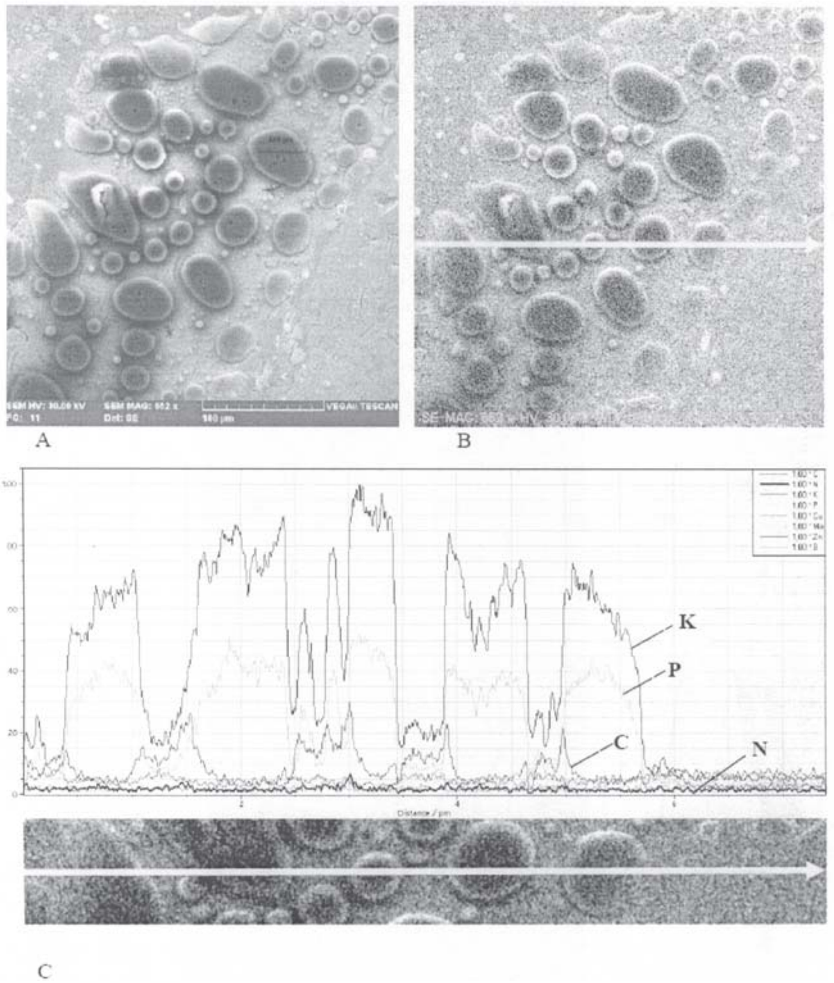


Fig. 12. Nutrinaft product full formulation (real emulsified.nutritive fluid) A) cast on nickel substrate. Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis

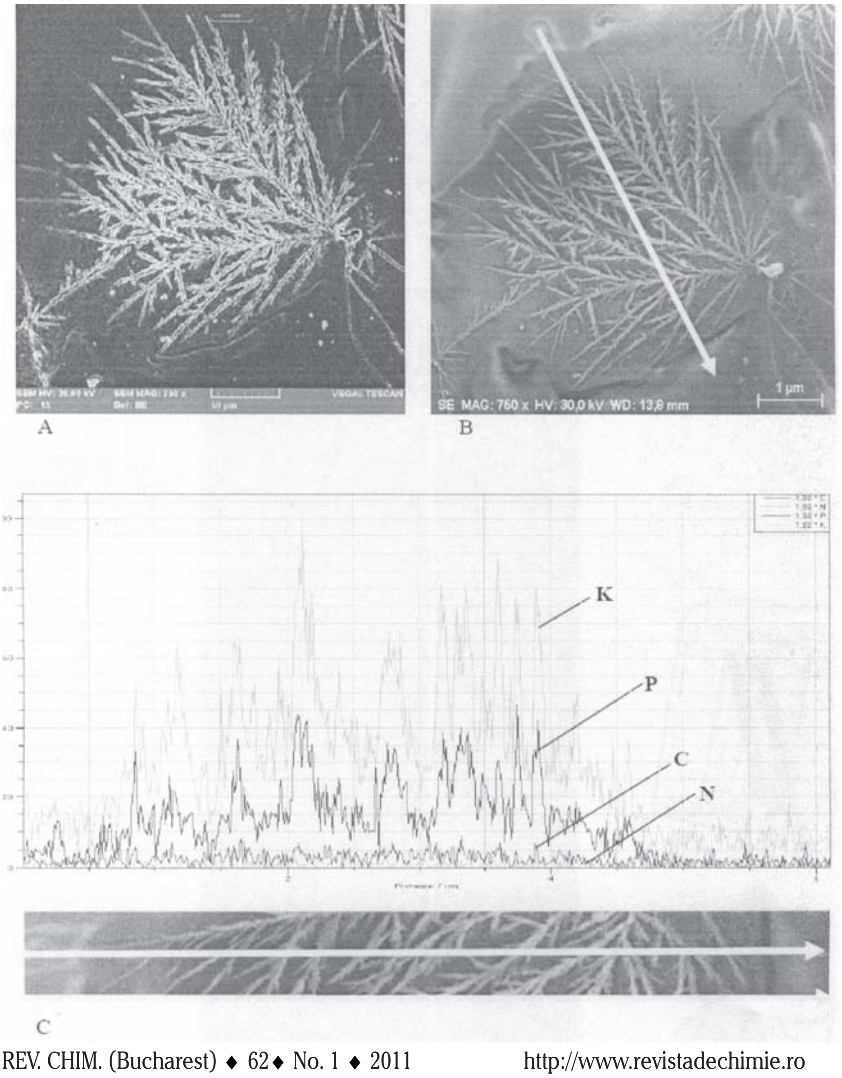
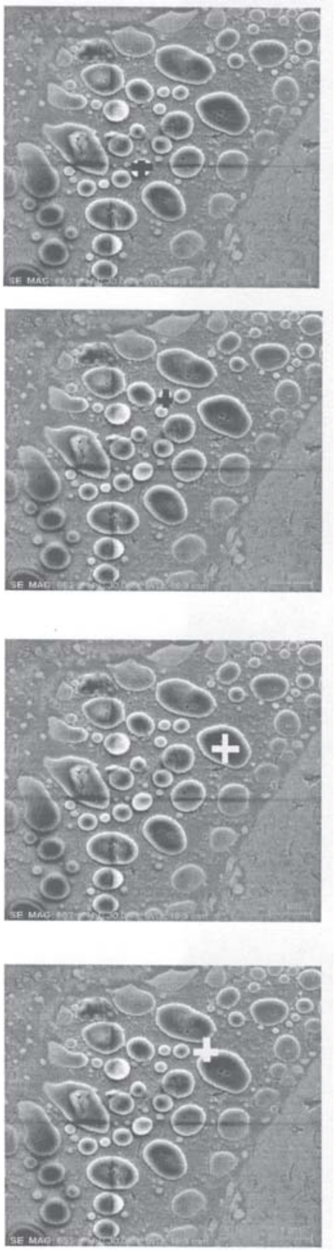


Fig. 13. Nutrinaft product full formulation (real mulsified.nutritive fluid) A) cast on glass substrate. Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis



```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]    [%]
---------------------------------------------
B   5  K-series   0,72     0,72     1,05   2,2
C   6  K-series   6,15     6,15     8,02   3,5
N   7  K-series  74,71    74,71    83,56  28,1
P  15  K-series   5,52     5,52     2,79   0,5
K  19  K-series   9,28     9,28     3,72   0,3
Cu 29  K-series   2,51     2,51     0,62   0,1
Zn 30  K-series   0,83     0,83     0,20   0,1
Mo 42  L-series   0,29     0,29     0,05   0,0
---------------------------------------------
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]    [%]
---------------------------------------------
B   5  K-series   0,93     0,93     1,35   2,5
C   6  K-series   7,04     7,04     9,18   3,7
N   7  K-series  73,38    73,38    82,06  27,7
P  15  K-series   5,08     5,08     2,57   0,4
K  19  K-series   9,87     9,87     3,96   0,3
Cu 29  K-series   2,62     2,62     0,65   0,1
Zn 30  K-series   0,84     0,84     0,20   0,1
Mo 42  L-series   0,25     0,25     0,04   0,0
---------------------------------------------
        Total: 100,00   100,00   100,00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]    [%]
---------------------------------------------
B   5  K-series   2,17     2,17     3,10   4,7
C   6  K-series   5,87     5,87     7,56   3,8
N   7  K-series  75,14    75,14    82,96  28,8
P  15  K-series   4,79     4,79     2,39   0,4
K  19  K-series   7,15     7,15     2,83   0,3
Cu 29  K-series   3,49     3,49     0,85   0,1
Zn 30  K-series   1,13     1,13     0,27   0,1
Mo 42  L-series   0,26     0,26     0,04   0,0
---------------------------------------------
        Total: 100,00   100,00   100,00
```

```
El AN Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]    [%]
---------------------------------------------
B   5  K-series   1,43     1,43     1,90   2,9
C   6  K-series  14,44    14,44    17,29   5,7
N   7  K-series  76,74    76,74    78,79  28,6
P  15  K-series   0,82     0,82     0,38   0,2
K  19  K-series   1,31     1,31     0,48   0,1
Cu 29  K-series   3,85     3,85     0,87   0,1
Zn 30  K-series   1,09     1,09     0,24   0,1
Mo 42  L-series   0,32     0,32     0,05   0,0
---------------------------------------------
        Total: 100,00   100,00   100,00
```

Fig. 14. Nutrinaft product full formulation (real emulsified.nutritive fluid). P\Local points compozition

composition as the little ones, with predominantly potassium and phosphorus accompanied by urea, but the inclusion of the micronutrients are more prominent than in the later case. Excepting molybdenum which is equally distributed between the two layers, the other micronutrients are more or less taken into top broken layer. The deeper layer, firstly separated in the substrate, contains less potassium and phosphorus (replaced by urea). In this layer the copper concentration is the highest and zinc and boron are preferentially captured. The composition of the two layers explains once again the above kinetic mechanism in the pellicular film precipitation.

Characteristics of the diluted Nutrinaft emulsions layer on solid surfaces were compared with layer characteristics of a typical foliar fertilizer formulated on the basis of urea-ammonium phosphates mixture. Figures 15 and 16 describe the chrystal structure and layering qualities of such a product. Firstly, urea and potassium phosphates form solid solution. Secondly, all these solid solutions are crystalline products, when they are precipitated from aqueous solutions. Their particulate layered structure is given in the figure 15A and 15B. Some distinctively crystalline acicular formation are randomly laying in some successive layers with a quite dense arrangement. Particularly, on the top if these layering formations, some globular crystals rich in of ammonium phosphates are discretely separated from the mass of the solid solution. Around these globular forms the crystalline mass has an increased content in phosphorus. At higher magnification the compact particle arrangement in crystalline layer is visualized in the figure 16. Large cracks and no porous structure are the only distinctive elements in the above figure. On small size surfaces cut on the top of solid solution layer, the distribution of element concentrations is very uniform.

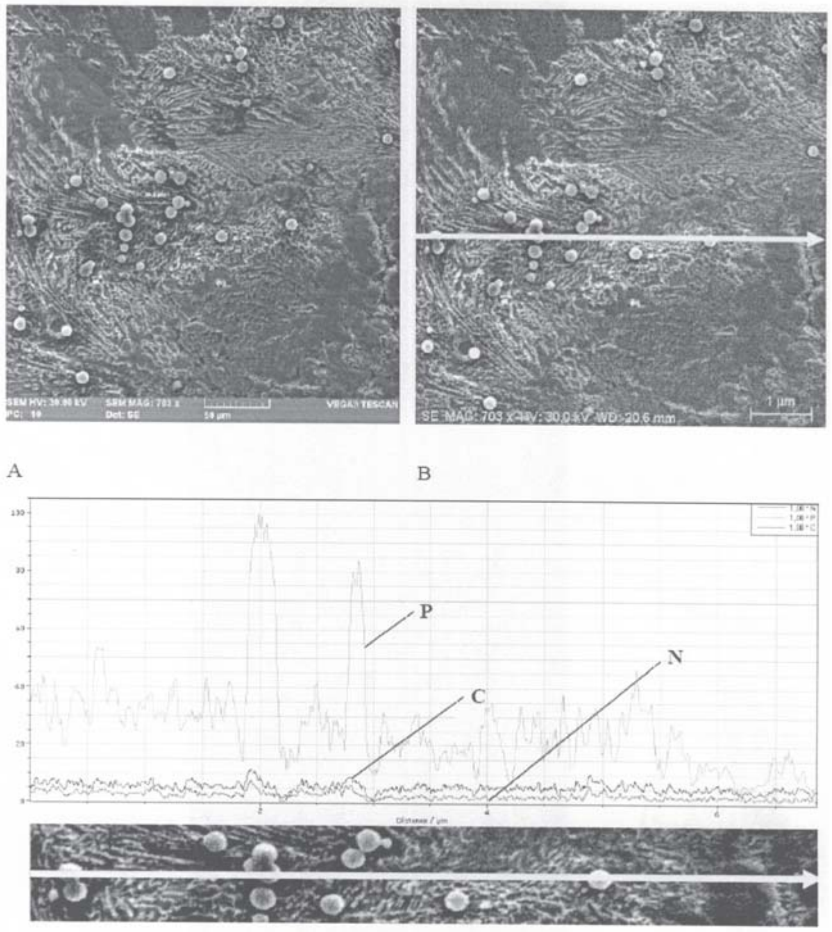


Fig. 15. Urea- Diammonium Hydrogen orthophosphate foliar fluid common formulation cast on nickel substrate. A) Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis

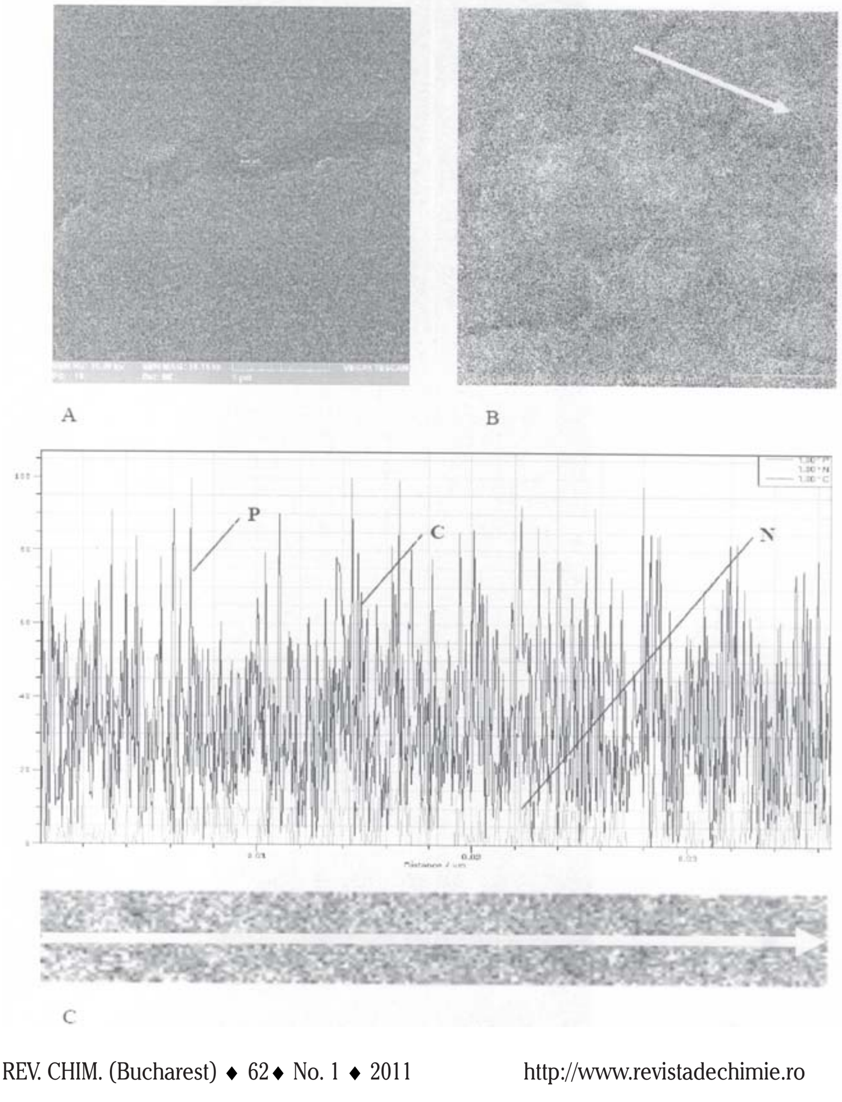


Fig. 16. Urea- Diammonium Hydrogen orthophosphate foliar fluid common formulation cast on glass substrate.A) Film particulate structure; B) Film thickness and elementary analysis composition profile; C) Profile EDX analysis

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Conclusions

An innovative concept in the formulation and properties design of nutritive emulsified fluids for agricultural use, originating from compulsory employment of both organic and inorganic components to achieve feeding, growth stimulating and plant protection, was developed on the ground of basic definitions of the carrier fluids transporting best lipophilic components and respectively best polar components through the cuticular membranes of plant foliage. Selection of each individual component has been made in good agreements with prominent attributes of the mechanism and kinetics of foliar absorption. It was shown that emulsified intermediaries, overbasic salts of naphthenic and oleic acid, enable not only the implementation of multifunctional biological performances, but also the best control of the foliar properties through hydrolysis, carbonation, layered foliar film precipitation and *p*H control.

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