

Preparation of Fertilizers with Rosin and Tricalcium Phosphate Coated Zinc Chelates. Laboratory Characterization

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Zinc fertilizers were obtained by adhering Zn-EDTA or Zn-lignosulfonate over urea pellets of 1.6–2 mm diameter, to give a span of zinc weight percentages between 0.60 and 1.40. Some of these pellets were also coated. The materials used as adhesives and coatings were mixtures of rosins (natural, dismutated, and esterified) and tricalcium phosphate. The weight percentages of coatings ranged from 0 to 47%. Water solubility kinetics showed that zinc solubilization in the base products (uncoated) were almost immediate, while the percentage released in the coated products diminished as the coating thicknesses were increased, up to 63 and 14% for the more heavily coated products of Zn-EDTA and Zn-lignosulfonate, respectively. Equations were established that enabled the behavior of products with the same percentage of coating in the two series to be predicted and compared. The tested products comply with national and international standards for commercial fertilizers with regard to their chemical composition. Their physical properties were within the limits found with commercial fertilizers. A scanning electron microscopy study showed that the rosin coatings were fairly compact and homogeneous.

Keywords: *Zinc chelate fertilizers; controlled release; rosin*

INTRODUCTION

Controlled-release (CR) technology was initially developed in the pharmaceutical and pesticide industries. Its application with fertilizers started later but is still thriving because slow-release fertilizers display the following advantages: (a) high efficiency in crops due to sustained correction of a mineral deficiency; (b) elimination of excessive uptake, preventing toxicities and damage to plants; (c) reduction of environmental damage by leaching or fixation losses; and (d) reduction of costs and risk of machinery damage to crops as the number of applications is diminished (Hignett, 1985; Jiménez et al., 1992; Joyce et al., 1993).

Although most products of this type found on the market provide macronutrients, this technology may be extended to fertilizers with micronutrients (Ray et al., 1993). This paper discusses products that gradually release zinc into the environment, through the adhesion to pellets of a commercial urea fertilizer (Silverberg et al., 1983) which were then given a protective layer of low solubility materials. These materials are used as a pelleted urea coating (Jiménez et al., 1992, 1993) and are formed by (1) a mixture of natural rosin (nonvolatile pine resin fraction), with rosins modified by dismutation and esterification to improve their stability, and (2) tricalcium phosphate.

Several materials have been used to obtain coated fertilizers: (a) inorganic materials, such as sulfur, phosphates, and silicates; (b) synthetic organic materials, for example dicyclopentadiene polymers (Osmocote), polyethylene, and ureic resins; and (c) natural organic materials, including rosin, rubber, and wax. To incorporate these materials into pellets, they are usually dissolved in toluene or, when necessary, fused. The resinic material employed for coating in this work was an inexpensive biodegradable product of natural origin, whose incorporation had the added advantage that it could be made from ethanolic solutions. Coatings with good plasticity and oxidation resistance were obtained with this mixture of modified resins. Furthermore, the

tricalcium phosphate employed in the mixture contributed to the reduction in the solubilization rate of the nutrients (Jiménez et al., 1992). Two commercial fertilizers in the form of chelates, Zn-EDTA and Zn-lignosulfonate (Zn-LS), were used as micronutrient sources.

Zinc emissions into water were assessed for all of the products prepared. The coatings that performed best were studied by electron microscopy and also underwent physical testing.

MATERIALS AND METHODS

Fertilizer Preparation. Two series of samples were prepared, using either Zn-EDTA or Zn-LS. Pelleted urea, previously sieved to between 1.6 and 2 mm, was placed into a 4 kg coating drum. A finely powdered zinc source, CTA (Zn-EDTA) or ISTARKA (Zn-LS) from Meristem (Spain), was added, and an adhesive mixture (1:1:1) of natural, dismutated (Residis), and esterified (Resiester T) rosins, provided by LURESA, dissolved in ethanol was added by spraying with a spray gun at regular time intervals. Excess solvent was removed through evaporation using a cold air current. Once the product was obtained with the required amount of zinc, it was successively coated with the mixture of rosins together with tricalcium phosphate, using the methodology proposed by Jiménez et al. (1984).

Zinc Emission. Zinc formulations (samples of 0.5 ± 0.001 g) were placed in triplicate in small, double-stoppered polyethylene bottles, and 10 mL of deionized water was added to each one. The temperature was kept constant by a thermostatically controlled bath (21 ± 1 °C). After certain intervals of time had elapsed, 5 mL of the floating solution was separated out and filtered. Zinc content in the filtrates was determined, and then 5 mL freshly distilled water was added to the residual suspension fertilizers.

Physical Tests. The methodology used in this paper was based on that proposed by the Tennessee Valley Authority (1970) and the International Fertilizer Development Center (1986). As proposed by these two bodies, the products selected for their kinetic behavior were subjected to the following tests: grain size, crushing strength, bulk density, and critical relative humidity and moisture absorption rate (stored at 88% relative humidity for 72 h).

Table 1. Products Prepared with Urea, Zn-EDTA Marketed as CTA or Zn-LS Marketed as ISTARKA, $\text{Ca}_3(\text{PO}_4)_2$, and a Mixture of Rosins

product	N (%)	Zn (%)	conditioner ^a (%)	coating		
				rosin (%)	tricalcium phosphate (%)	total
Zn-EDTA-0 ^b	38.64	1.40	5.86			
Zn-EDTA-1	35.42	1.23	5.50	6.31	2.32	8.63
Zn-EDTA-2	31.28	1.07	5.00	14.2	5.01	19.2
Zn-EDTA-3	24.38	0.96	3.99	25.1	11.0	36.1
Zn-EDTA-4	20.70	0.60	3.21	32.5	14.6	47.1
Zn-LS-0	39.10	1.27	9.23			
Zn-LS-1	34.04	1.20	8.03	7.13	5.39	12.5
Zn-LS-2	30.36	1.08	7.17	12.9	9.03	21.9
Zn-LS-3	26.22	0.89	6.19	21.8	11.0	32.8

^a Binding material used, conditioner, s and impurities in the initial commercial products. ^b The number gives the respective order of each product in the series according to the total amount of coating.

The coating was also studied by photomicrography. Pellets were split in half and the fractions secured to sample holders with carbon LIT-C glue and were metal coated with a 60 nm layer of platinum using an SEM Coating UNIT PS-3 metal coater. Micrographs at different magnifications were taken with a Hitachi Model S-2500 electron scanner microscope.

Analysis Methods. Nitrogen was determined in keeping with the sample characteristics either by a spectrophotometric method using *p*-dimethylaminobenzaldehyde in a hydroalcohol medium with hydrochloric acid as reagents (Ministerio de Agricultura, Pesca y Alimentación, 1994) and using a Shimadzu UV-160 apparatus or according to the Kjeldhal method (Association of Official Analytical Chemists, 1990) using a Tecator Kjeltac 1026. Rosin percentages were usually determined by differences between the total and the sum of the rest of the components. The validity of these calculations was further verified by UV-visible spectrophotometry determinations (the three rosins were evaluated together due to their similarity with regard to absorption bands, as well as their solubility in organic solvents). The mixture of the three rosins, dissolved in benzene, gave a maximum at 279 nm. Under these conditions other fertilizer components do not interfere in the measurement. Zinc and calcium were determined by atomic absorption spectrophotometry (Perkin-Elmer Model 3300).

RESULTS AND DISCUSSION

Composition of the Fertilizers. Products with zinc adhered onto urea ("0" of each series) and with different percentage coatings were produced. The range of zinc percentages were from 1.40 to 0.60 for the Zn-EDTA series and from 1.27 to 0.89 for the Zn-LS series, with coefficients of variation from 2 to 3%. The weight percentage coatings were 8.63–47.1 and 12.5–32.8 for the Zn-EDTA and Zn-LS series, respectively, with coefficients of variation from 5 to 6%. Their compositions are shown in Table 1. All products complied with national (*Bol. Of. Estado*, 1994) and international regulations (*Diario Of. Comunidades Eur.*, 1989) on the permitted concentrations of micronutrient.

Study of Zinc Emission into Water. Figures 1 and 2 show the percentage of zinc solubilized as a function of time for the first 10 days. Over the following days curves showed analogous trends, with the Zn-EDTA fertilizers almost completely solubilized by the end of 1 month. With the uncoated base products (Zn-EDTA-0 and Zn-LS-0), zinc was solubilized in the first few hours, while in the coated products of both series, this occurred slowly throughout the test. Moreover, solubilization diminished considerably with the increase in coating percentage since the coating became more even and

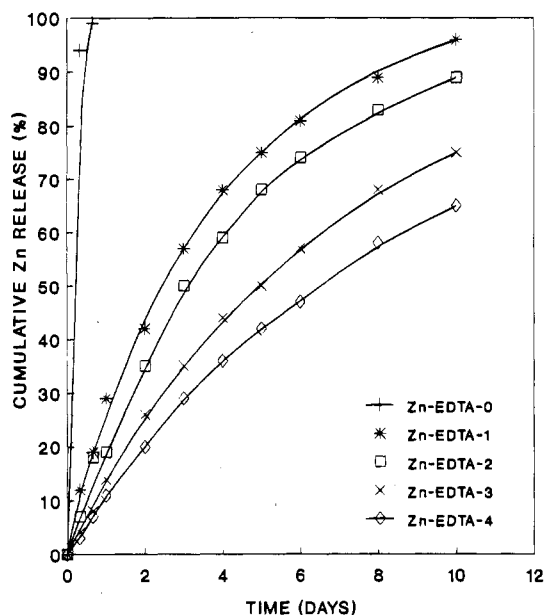


Figure 1. Cumulative zinc release (percent) from Zn-EDTA prepared formulations.

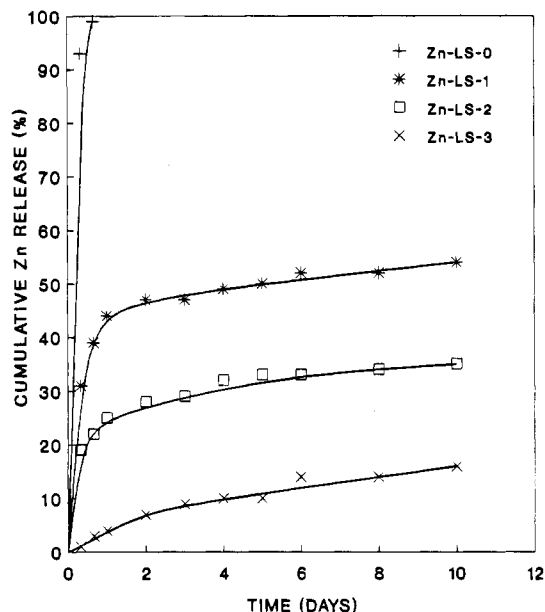


Figure 2. Cumulative zinc release (percent) from Zn-LS prepared formulations.

displayed fewer pores and defects, as shown from the micrographs.

Solubilization curves for coated Zn-LS products displayed two areas of different behavior: the first, more rapid, release until approximately mid-day and the second, slower. The slow-release fraction increased as the proportion of coating rose, up to the point where, in the case of Zn-LS-3, the two sections were indistinguishable. In Zn-EDTA products, release was slow and progressive from the beginning and these two areas were not observed in the curves.

The micronutrient solubilization process occurs via diffusion through the fertilizer's protective coating. The rate declines with time, being proportional, in most cases, to the amount of zinc still present in the fertilizer. Thus, zinc release could be represented by a first-order kinetics equation (Collins, 1983). If the percentage nonsolubilized in time *t*, compared to the initial concentration, is designated *I* and the solubility rate

Table 2. Results Obtained by Simple Linear Correlation for the Coated Zn-EDTA and Zn-LS between $\ln I$ and the Time in Days

product	coating (%)	k (days ⁻¹)	$\ln I_0$	r^a
Zn-EDTA-1	8.63	0.300	4.63	-0.99***
Zn-EDTA-2	19.2	0.219	4.59	-0.99***
Zn-EDTA-3	36.1	0.139	4.60	-0.99***
Zn-EDTA-4	47.0	0.105	4.59	-0.99***
Zn-LS-1	12.5	0.032	4.10	-0.86**
Zn-LS-2	21.9	0.020	4.34	-0.89***
Zn-LS-3	32.7	0.016	4.57	-0.96***

^a Coefficient of simple linear correlation. ***, ** Significant at $P < 0.001$ and 0.01 levels, respectively.

constant k , the equation is $\ln I = \ln I_0 - kt$, where I_0 must be 100 ($\ln I_0 = 4.6$). By calculating the $\ln I$ values as a function of time t and using linear regression analysis, the values of the slopes and ordinates at origin were obtained with acceptable correlation coefficients and probability levels. As calculated values of the intercept were for some products smaller than 4.6, $\ln I_0$ was defined as the intercept of the regression equations obtained (Table 2). The interpretation of this behavior was that, due to the nature of the coatings and the source of adhered zinc, there may have been a variable amount which was immediately solubilized and, therefore, first-order kinetics were not strictly followed. The latter occurred particularly in the least coated Zn-LS products (Zn-LS-1 and -2), for which the coefficients of correlation were less than the rest.

Rate constants diminished when the percentage of coating increased and while all are small, those of the Zn-EDTA series are almost 10 times greater than those of the Zn-LS series in products with similar percentages of coating. Therefore, diffusion of Zn-EDTA was faster than that of Zn-LS. This demonstrated the importance of the zinc complex used.

To quantify the influence of the coating on the rate of release, relations between k and the percentage of coating were established:

Zn-EDTA series

$$k = 5.10 \times 10^{-3} (\%C) + 0.330, r = -0.98$$

(significant at $P = 0.01$)

Zn-LS series

$$\ln k = 0.746 \ln(\%C) - 1.55, r = -0.99$$

(significant at $P = 0.05$)

The zinc release rate of any product was fairly accurately predicted with the equations obtained, provided the same methodology, conditions, and sources of micronutrients were used. The slopes of both equations show that when coating percentages were increased, the rate of solubilization decreased. Further information

in the evaluation of fertilizers can be gained from the different behavior observed in the first period of solubilization. I_0 depended on the $\%C$ of the fertilizer with a coating percentage smaller than 33% at which it is taken as 100. To quantify the amount of zinc released immediately from the Zn-LS series, the following equation was established:

$$I_0 = 1.79 (\%C) + 34.48, r = 0.99$$

(significant at $P = 0.05$)

I_0 increased when $\%C$ increased due to the positive slope. Thus, the use of high weight percentages of coating was desirable to avoid rapid solubilization after the initial fertilizer application.

Physical Tests. To perform the physical tests required for these types of fertilizers, samples 2 and 3 were selected from each series. These materials had similar percentages of coatings, and their I_0 values were less than 100 in only one case ($\approx 77\%$). Although Zn-EDTA-4 had satisfactory kinetic behavior, due to the slow solubilization of zinc, it was estimated that the results obtained with Zn-EDTA-2 and Zn-EDTA-3 could be extrapolatable to it and that its coating could be excessive, both as far as a reduction in the nutrient percentage was concerned and for cost considerations.

Grain Size. The grain size composition of the tested products is expressed in percentages retained in each sieve (Table 3). In all cases at least 97% of the pellets was between 1.0 and 4.0 mm (specifications are $>85\%$). The small percentage of pellets less than 1.6 mm may appear because there was some fracture, but most of them were larger than 1.6–2 mm. Moreover, size increased initially when the micronutrient was added and subsequently with the coating. However, the fraction greater than 3.2 mm was very small or negligible, even in products with the thickest coating.

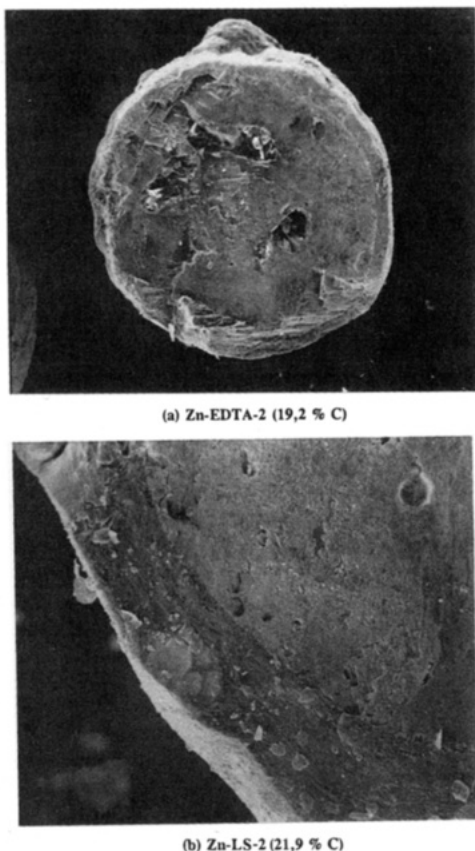
Crushing Strength. The values obtained (Table 3) in uncoated products were 10% greater than the control (urea pellets). It is important to avoid breakage and strain of pellets during manufacture and transport. In coated products strength increased with the coating. Thus, rosin-tricalcium phosphate coatings produce a major increase in the grain's hardness, giving the Zn-EDTA-3 product a strength 1.8 times greater than that of the control.

Bulk Density. Although, as can be seen from Table 3, the bulk density decreased very slightly when the micronutrient was adhered to the base product, it increased a little in each series compared to that of the uncoated base products. Products with similar coating percentages displayed similar bulk densities. The determination of bulk density is required for bag sizing, capacity of storage, and transport. All of the products had bulk densities within the usual range for pelleted

Table 3. Results Obtained for Grain Size, Crushing Strength, Bulk Density, and Moisture Absorption

product	% of fraction size			crushing strength (kg/grain)	bulk density (g/cm ³)	moisture adsorbed (%) at 21 °C, 88% RH		
	2.5–3.2 mm	2.0–2.5 mm	1.6–2.0 mm			24 h	48 h	72 h
control ^a	1	18	65	0.96	0.71	14.0	16.9	20.2
Zn-EDTA-0	6	48	38	1.07	0.70	16.4	19.9	23.5
Zn-EDTA-2	18	56	24	1.29	0.74	5.5	7.3	9.2
Zn-EDTA-3	40	57	1	1.79	0.77	4.9	5.5	6.5
Zn-LS-0	5	32	55	1.05	0.70	15.7	19.2	22.6
Zn-LS-2	7	63	29	1.31	0.76	5.1	6.3	8.1
Zn-LS-3	19	69	9	1.65	0.77	4.8	5.6	6.3

^a Pelleted commercial urea.



(a) Zn-EDTA-2 (19,2 % C)

(b) Zn-LS-2 (21,9 % C)

Figure 3. Cross-sectional micrographs of coated pellets: (a) Zn-EDTA-2 (36 \times); (b) Zn-LS-2 (150 \times). (The figure is reproduced here at 50% of the original.)

fertilizers, which lie between 0.72 and 1.20 g/cm³ (Hignett, 1985).

Relative Moisture Absorption. Even though moisture absorption commences for urea at 80.5% relative humidity (Hoffmeister, 1979) and for uncoated Zn-EDTA-0 and Zn-LS-0 products at 70.4% relative humidity (about 5% after 72 h), for coated products to absorb significant amounts of water the relative humidity must be maintained at $\geq 88\%$. For fertilizers, a relatively high critical humidity is an advantage for handling and packing. The amount of water absorbed by coated products was far less than that of uncoated products and commercial urea and decreased as the coating thickness was increased (Table 3). Similarly, the moisture absorption rate also decreased with the rise in percentage coating. This behavior is very convenient for structural stability.

Photomicrographic Study of Granules. Micrographs taken of the uncoated products (Zn-EDTA-0 and Zn-LS-0) were of little interest, because only a fine film formed as a result of adhering the material containing the micronutrient in successive operations was observed, whose structure was not compact. Figure 3 relates to coated products, two from each series. Two areas were observed in all of the micrographs but particularly at the highest magnifications: the inner region made up of urea and the outer resin coating with the micronutrient. The coatings appeared to be compact and quite homogeneous, although some defects such as pores or tiny cracks were seen which, in general, did not communicate the grain's interior directly with the exterior. The coatings were joined to the urea support

Table 4. Average Coating Thickness

product	av thickness (μm)	SE	confidence intervals (95%)
Zn-EDTA-2	96	3.15	89–103
Zn-EDTA-3	168	4.38	159–179
Zn-LS-2	101	5.49	88–113
Zn-LS-3	155	6.15	141–169

without any substantial fractures. No differences were observed between the two series. Small differences that may appear could result from sample cut, the angle of view, and lighting.

Average product coating thickness values were established from the micrographs (Table 4). These results demonstrated that the thickness was greater as the coating proportion increased and similar coating percentages related to similar average thicknesses.

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