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FERTILIZER WITH HUMIC SUBSTANCES

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ABSTRACT

For the purpose of having it licensed in Romania, the Folhum fertilizer was tested in the vegetation house and in field, with the result of a distinctly significant yield increase.

The liquid fertilizer was obtained by neutralizing phosphoric acid of 85% concentration with potassium carbonate of 98% concentration. The reaction took place under permanent stirring at the temperature of 250-300°C, and by gradually adding a source of nitrogen (amidic, nitric and ammoniacal), a solution of microelements (Fe, Cu, Zn, Mg, Mn, B) chelated with Na2EDTA and a solution of potassium humate. Potassium humate was extracted from lignite with a potassium carbonat solution.

Experiments were organized in three climatic areas, vegetation house, greenhouse and field, in the Teleorman and Iasi districts. The experimental fertilizer application provided increases of the yield by 45.5% in the Dacia Pontica tomato and 49.2% in the Justin sunflower in vegetation house, as compared to the control to which foliar fertilizer was not applied. The application of Folhum in field increased by 14.4% the yield of sunflower with basic fertilization 80 kg N/ha, 80 kg P_2O_5 /ha, as compared to the control alternative to which foliar fertilizer was not applied. It increased the yield of tomato hybrid ADI 7 grown in the greenhouse with drip irrigation on a non-fertilized soil by 38.5%, and by 34.9% the grape yield in a Chasselas Doré variety vine culture. All yield increases were statistically significant at P<5%.

Based on these increases, the fertilizer was authorized as RO-FERTILIZER and it may be used in Romania.

Key words: heritability, nitrogen nutrition efficiency, variability, wheat.

INTRODUCTION

Fertilizers containing humic substances can be combined in different proportions with nutritive elements (U.S. Patent 20100275663, U.S. Patent 20080121005), as well as with other organic natural or synthetic substances (U.S. Patent 7947818).

Humic fertilizers contain a series of essential elements in the form of humates extracted from coal mass in complex NPK-type matrices which, after their incorporation in the soil, ensure the assimilation of the nutrient ions contained and intensify the nutrition process (Cioroianu et al., 2009). The fertilizers with humic substances can prevent the loss of nitrogen by levigation, both in clayey and sandy soils, by their retention. The organic matter and the humic substances are at the same time the energetic substrate of the microflora activity in the rhizosphere and represent an important reservoir of chelate-type compounds, which have a great capacity to bind various metal ions (B, Cu, Ca, Fe, Mg, Mo, Zn) and to form organo-metallic complexes with an important role in the formation of the soil characteristics and plant nutrition. A large number of nutritive ions (PO_4^{3-}; SO_4^{2-}; Zn^{2+}; Cu^{2+}; Fe^{2+}; Ca^{2+}; Ca^{2+}) are retained by chelating processes, in the form of compounds of various solubility.

As compared to EDTA, the humic substances are compatible with the plant and non-toxic both to the plant and to the environment (US Patent 7947818/2011). In the specialized literature there are numerous examples of heteromolecular structures with a fertilizing role, obtained by chelating meso- and microelements with organic macro-molecules of the type of humic extracts (US Patent 6080220/2000).

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For the humic acids, the average chemical formula $C_{187}H_{186}O_{89}N_9S$ is accepted. An approximately equal H : C ratio indicates a significant degree of the aromatic character (the presence of benzene rings in the structure), while the low oxygen level, namely the subunitary O : C ratio, indicates fewer functional acid groups that the ones in the fulvic acids.

The functional groupings of the humic substances act as acids or bases, as anion and cation changers and specific absorbent for the nutritive and harmful substances (Berca, 2011). Extraradicular application of the fertilizers containing organic substances with meso- and microelements (B, Cu, Co, Fe, Mg, Mn, Mo, S, Zn), when made in the specific growing periods, represents a high technique for optimisation of the nutrition and health condition of the plants, but also for the quality increase.

In Romania, although there are many coal deposits, their value as nutritive substances for the plants or for the improvement of the degraded soils has not been exploited. The quality and quantity of humic substances extracted depends of the source of the coal used, but also on the extraction procedure.

The novelty of the research consists in the elaboration of an original technology for the extraction of the humic acids from the indigenous coal, their complex characterization and obtaining of fertilizers with a complex matrix which bring together macro-, meso- and microelements and humic substances, as well as their testing by foliar application in the pedo-climatic conditions of Romania.

This paper presents the way to obtain a liquid fertilizer with humic substances, and the results of the tests that showed the influence of this fertilizer on the production of tomatoes and sunflower cultivated in vegetation houses and in experimental field tests.

MATERIAL AND METHODS

The procedure to obtain the liquid fertilizer consisted in the neutralization of the phosphoric acid concentration of 85% with potassium carbonate concentration of 98%, resulting in a solution that contained mono- and dipotassium phosphate. The reaction took place under a continuous stirring at a constant temperature of 250-300°C, gradually adding an amidic, nitrate and ammonium nitrogen source, and maintaining the reaction temperature, and as a result a complex mixture of macro-elements was obtained. Under continuous stirring conditions, at a temperature of 25-30°C, a solution of microelements (Fe, Cu, Zn, Mg, Mn, B) was chelated with EDTA disodium salt and mixed with a solution of potassium humate (Figure 1).

The method of extracting humic substances from lignite was the alkaline extraction, followed or not followed by a dewatering and/or ennoblement with salt containing nutrients. Within the experiments performed, the potassium humate used to obtain the fertilizer was extracted from coal mass, lignite, with a potassium carbonate solution. In order to validate the operation technologies and to define their parameters, after establishing the technological flow schemes for obtaining fertilizers, experiments were performed in a 1000 cm^3 stainless micro-installation coupled to an ultra-thermostat equipment for recirculation of the heating/cooling agent, able to adapt and maintain the reaction temperature in the 0-100°C range, with a deviation of ±0.5°C. The technical procedures used to verify and validate the technologies for obtaining the fertilizer focused on the classic physical and physical-chemical processes, without the involvement of the synthesis reactions, namely: dosage, dissolution, homogenisation, chelating, extraction - complexion, ion exchange, concentration correction, settling/sedimentation and filtration.

In order to establish the operating parameters to elaborate the mass balance schemes, were carried out analysis hourly, after 24 and 36 hours respectively, within the phases of processes.

The potassium humate extracted from lignite and used for obtaining the experimental fertilizer was thermally analysed in the temperature range: environment temperature – 1000°C, in the air, with a heating speed of

10 K/minute, the TG (Thermogravimetric Analysis), DTG (Deriva-tive Thermogravimetric Analysis), DTA (differrential thermal analysis) and DSC (Differential Scanning Calorimetry) curves being simultaneously traced (Sîrbu et al., 2010). The measurements were made by means of a Perkin Elmer thermo balance which enabled mass determinations with a 1-2% error in the temperature range: environment temperature – 1400°C and a heating speed of 0.1 - 50 K/minute.

The spectral analysis of the humic substances was made by Fourier transform infrared spectroscopy (FTIR), by means of the PerkinElmer Spectrum 1000 spectrometer and the VERTEX 70, in the wave length range of 650-4000 cm^{-1}.

All the spectra were obtained by using the total reflection in infrared with the ATR module. The resolution was 4 cm^{-1}, with 32 scans and the correction of the CO_2 and H_2O, in transmittance mode.

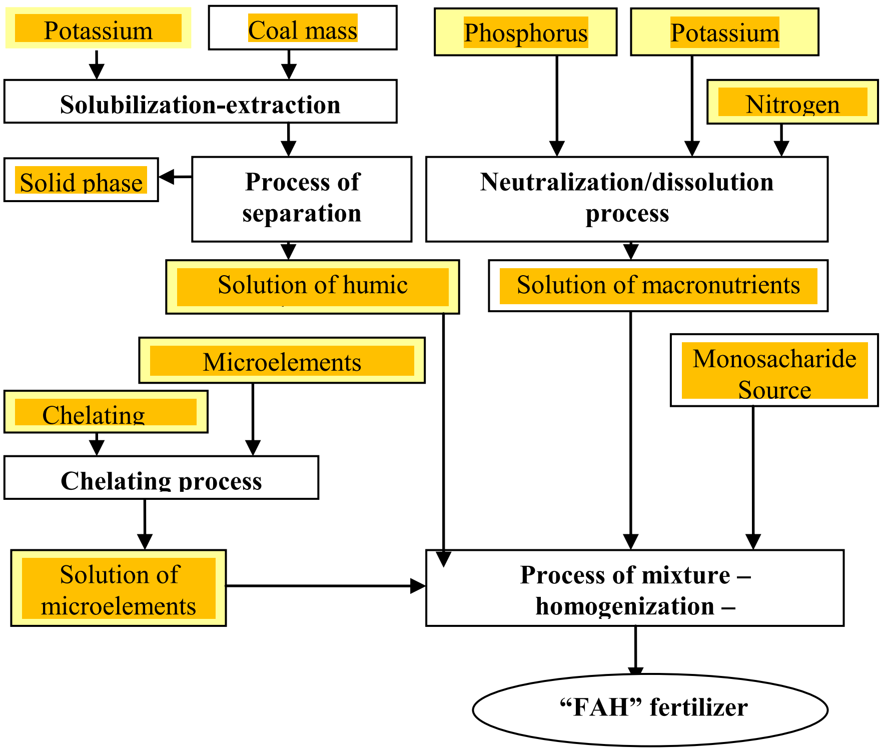

Figure 1. General scheme to obtain the NPK-type fertilizer with humic substances

RESULTS AND DISCUSSION

The potassium humate obtained in the laboratory by alkaline extraction from lignite consisted of four main decomposition stages, namely: up to 85.3°C, 10.4% loss, the stage corresponded to drying by an endothermic process with 57.9 J/g enthalpy; the second process – still endothermic – took place in the 85.3267°C with an 11.6% mass loss and a 145.5 J/g process enthalpy. In the range of 267-600°C the mass loss was 5.4% when a slight exothermic effect took place with a 58.3 J/g enthalpy, the maximum heat emitted being at 419.8°C for a heat flow of 1.12 mW. The fourth stage of decomposition was recorded between 600 and 800°C, with a 4.7% mass loss. The humic/fulvic mixture present in the fertilizer matrix contained about 70% organic acids, whereof 50% derived from the humic acids and 20% from the fulvic acids.

Figure 2 presents the spectrum in infrared obtained for the humic acid extracted from the coal mass and Table 1 presents the assignment of the wave lengths identified (Hyun Sang Shin et al., 1994; Giovanela et al., 2004).

The humic acid obtained and used in performing the experiments had a relatively limited and well localized wave length spectrum, corresponding to the carboxylic and aromatic groups as well as to the aliphatic compounds.

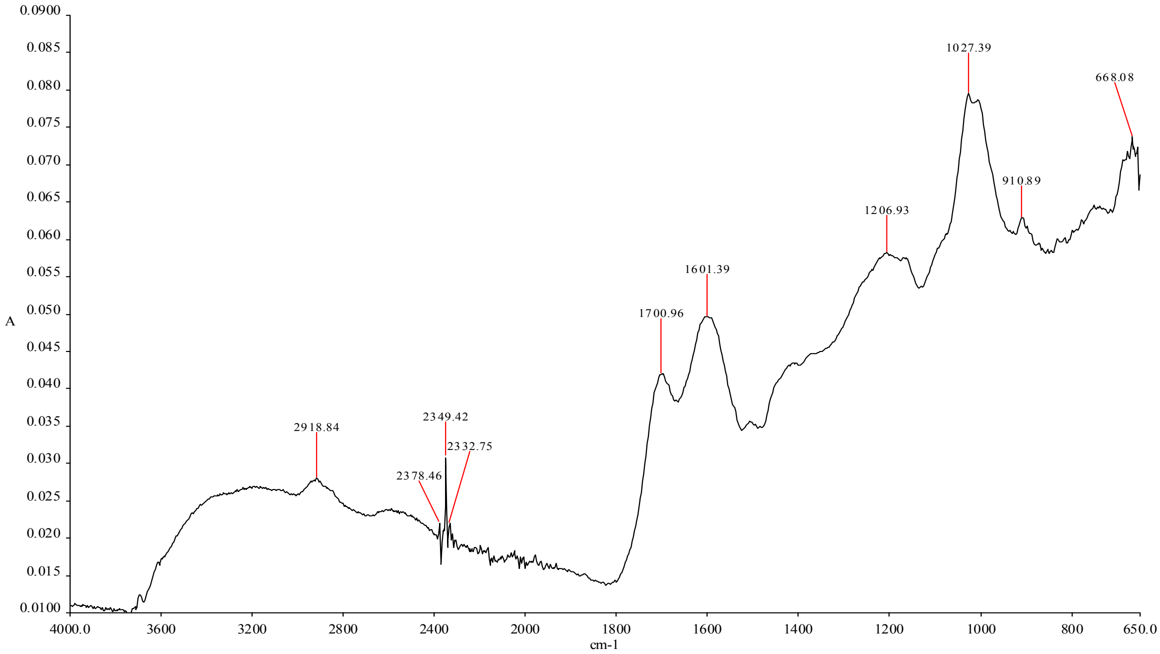

Figure 2. FT-IR image of the humic acid extracted from the coal mass (lignite)

Table 1. FTIR characterization for the humic acids

Wavelength (cm^{-1})	Attribution	Feature
2920	Anti-symmetric CH_2	-
2850	Symmetric CH_2	-
1720-1707	C=O stretch of COOH or COOR	Free organic acids, Carboxylic acids, aromatic esters
1650-1600	Aromatic C=C stretching and/or asymmetric C-O stretch in COO-	Aromatic or aliphatic carboxylates
1426	Symmetric C-O stretch from COO- or stretch and OH deformation (COOH)	Carboxylate/Carboxylic structures (humic acids)
1265 (approximately)	C-O stretching of phenolic OH and/or arylmethylethers	Indicative of lignin backbone
1080-1030	Combination of C-O stretching and O-H deformation	Polysaccharides, alcohols and carbohydrates

The physicochemical characteristics measured for the "FAH" experimentally obtained fertilizer with humic acids are shown in Tables 2 and 3.

Table 2. Measured physical characteristics for "FAH" fertilizer solution

No.	Fertilizer solution concentration (%)	Physical characteristics	
		pH (units of pH)	Conductivity (microS/cm)
1	Solution concentration 5%	7.31	4880
2	Solution concentration 1%	7.22	1362
3	Solution concentration 0.5%	7.16	958
4	Solution concentration 0.25%	7.12	714

Table 3. Control fertilizer “F111”, FKH and FAH composition characteristics

No.	Determined component	F111	FKH	FAH
		Determined value (%)	Determined value (%)	Determined value (%)
1	Total nitrogen, N	9.37	0.18	20.28
2	Phosphorus, P_2O_5	8.64	0.01	3.63
3	Potassium, K_2O	7.55	0.85	3.89
4	Boron, B	0.025	0.021	0.010
5	Cobalt, Co	0.01	0.003	0.003
6	Copper, Cu	0.023	0.018	0.028
7	Iron, Fe	0.048	0.021	0.039
8	Magnesium, Mg	0.038	0.038	0.018
9	Manganese, Mn	0.031	0.012	0.021
10	Molybdenum, Mo	0.01	0.003	0.003
11	Sulfur, S	0.18	0.23	0.14
12	Zinc, Zn	0.025	0.018	0.019
13	Organic substances, of which:	2.20	4.25	6.30
	Humic acids	-	0.72	0.82
	Active ingredient	28.15	5.65	34.38

The experiments were performed in Mitscherlich vegetation pots filled with 20 kg of soil, in three repetitions for each fertilized variant, including the non-fertilized control. The agrochemical experiments on Justin sunflower and on Dacia Pontica tomato were conducted on a soil made up of vermic chernozem with the following characteristics: 3.36% humus, 0.22% nitrogen, 88 ppm mobile phosphorus (P soluble in AL) and 280 ppm mobile potassium (K soluble in AL) and a slightly alkaline pH of 7.4 units.

The experimental fertilizers were applied as a 1% solution in the amount of 30 ml/pot, in 3 treatments every 10-15 days. The first application was performed when plants were 30-35 cm in height.

In the agrochemical experiments, with the experimental fertilizer (FAH) testing, 3 controls were used: one control (M0) without extraradicular fertilization, one control represented by a foliar fertilizer used in classical agriculture (F111) and one control represented by a potassium humate with microelements (FKH). The characteristics of the fertilizers used in the experiments, i.e. F111, FKH and FAH are shown in table 3.

The data obtained were statistically processed by using the Least Significant Differences (LSD) test for a 95% confidence level.

In case of the experiments performed with the Dacia Pontica tomato cultivated in pots, following the extraradicular application of the fertilizer with humic substances, the yield increased by 45% as compared to the control to which no foliar fertilizer was applied (M0), by 4% as compared to the F111 control and by 34% as compared to the FKH control. The yield obtained by application of the fertilizer distinctly and significantly differed from the control to which no foliar fertilizer was applied (M0) and (FKH) and significantly differed from the F111 control.

In case of the experiments performed with the Dacia Pontica tomato cultivated in pots (Table 4), by the extraradicular application of the fertilizer with humic substances, the yields obtained for the fertilized variants were significantly higher as compared to the control to which no foliar fertilizer was applied (M0).

The difference of the yield obtained by the application of the fertilizers containing humic substances (FAH) in addition to the N, P, K nutrients, as compared to the variant containing only mineral substances (F111) was positive and significant.

Table 4. Dacia Pontica tomato yield

Fertilization variant	Tomato yield, (g/plant)	Significance
Control M0	771.3	a
FKH	835.7	b
F111	1079.7	c
FAH	1121.7	d
LSD5%	30.6	

In the experiments performed with sunflower cultivated in pots, following the extraradicular application of the fertilizer with humic substances (FKH), the yield of the foliar fertilized variants was significantly higher than that of the control to which no foliar fertilizer was applied (M0) (Table 5).

The extraradicular application of the fertilizer with humic substances resulted in a yield 49.2% higher than that of the control to which no foliar fertilizer was applied (M0), similar with the yield obtained with application of F111 fertilizer.

Table 5. Sunflower seed yield

Fertilization variant	Sunflower seed yield (g/plant)	Significance
Control M0	46.6	a
FKH	57.8	b
F111	71.9	c
FAH	69.6	c
LSD5%	7.1	

A field test of the FAH (Folhum) foliar fertilizer in sunflower was performed at the Agricultural Research and Development Station Teleorman, on a fertile cambic chernozem soil (humus 3.5%, Nt 0.170%, PAL 50 ppm, KAL 300 ppm, V% - 81%, pH - 6.2). The following technology was applied: ploughing in autumn 2010, disc harrowing, cultivation in spring, sowing on 7 April 2011 of hybrid Favorit. Harvesting took place in the last decade of August.

The weather conditions were favourable for the productive potential of the sunflower crop. The average temperature of the period 1 October 2010 - 30 September 2011 was 11.3°C, 0.4°C higher that the multiannual average temperature. In the last decade of the month of July until mid September the absolute highest temperature was 37.9°C and the absolute minimum temperature was 17.8°C. Rain fell in excess throughout the period (143.6 mm), but it was scarce in August - September, which was highly favourable to sunflower.

It rained in the vegetation stages when water consumption was high, favouring formation of high seed yield, which influenced the effect of the foliar fertilizer applied.

The fertilizer was applied on the foliage in 2 treatments, in the form of 0.5% diluted solutions, 1000 l of diluted solution ha^{-1} in each treatment.

Table 6. Effect of Folhum (FAH) fertilizer applied to sunflower with a previous basic fertilizer ($N – 80\ ha^{-1}$; $P_2O_5 – 80\ kg\ ha^{-1}$)

No.	Treatment*	Number of applications	Solution concentration (%)	Quantity of fertilizer used ($l\ ha^{-1}$)		Seed yield ($kg\ ha^{-1}$)	Yield increase		
				For one application	For all applications		$kg\ ha^{-1}$	%	Per l of foliar fertilizer
1	Control	-	-			2742	-	100.0	-
2	FAH	2	0.5	5.0	10.0	3136	394	114.4	39.4
LSD	5%					284			
	1%					358			

The foliar fertilization with Folhum applied to sunflower in a soil with previous basic fertilization with $N – 80\ kg\ ha^{-1}$ and $P_2O_5 – 80\ kg\ ha^{-1}$ resulted in a yield increase of 394 $kg\ ha^{-1}$ seed, as compared to the control to which no foliar fertilizer was applied (Table 6).

A monofactorial experiment was placed in the greenhouse at ICB Iasi, in randomised blocks, on a cambic chernozem soil, using tomato hybrid ADI 7. Planting took place on 14 April 2011 and harvesting on 1 August 2011 (Table 7).

The Folhum fertilizer was applied on foliage in 3 treatments, in a 0.5% concentration and in a quantity of 1000 l of diluted solution per hectare in each treatment.

The average temperature of the period 1 October 2010 - 30 September 2011 was 9.2°C as compared to the normal annual average temperature of 9.6°C. In the vegetation period of April – September, the average temperature was 22.6°C, 5.3°C higher than the normal average temperature, which is 17.3°C.

The higher temperatures in the vegetation months were favourable to tomatoes and vine cultures experimented in the field. The rainfalls in 2010-2011 were scarce (444.4 mm), as compared to the multiannual average (517.8 mm). The rainfall during the vegetation period was 272.4 mm, as compared to the normal for the same period, which is 294.7 mm.

Table 7. Effect of FAH fertilizer applied to tomatoes (hybrid ADI 7) grown at ICB Iasi in greenhouse with drip irrigation, on a soil without previous basic fertilization

No.	Treatment*	Number of applications	Solution concentration (%)	Quantity of fertilizer used ($l\ ha^{-1}$)		Fruit production ($kg\ ha^{-1}$)	Yield increase		
				For one application	For all applications		$kg\ ha^{-1}$	%	Per l of foliar fertilizer
1	Control	-	-			44805	-	100.0	-
2	FAH	3	0.5	5.0	15.0	62041	17236	138.5	1149.0
LSD	5%					6659			
	1%					10184			
	0.1%					13782			

Table 8. Effect of FAH fertilizer applied to vine, Chasselas Doré variety, grown on cambic chernozem, at the ICB Iasi, without previous basic fertilization

No.	Treatment*	Number of applications	Solution concentration (%)	Quantity of fertilizer used ($l\ ha^{-1}$)		Grape production ($kg\ ha^{-1}$)	Yield increase		
				For one application	For all applications		$kg\ ha^{-1}$	%	Per 1 of foliar fertilizer
1	Control	-	-			11213	-	100.0	-
2	FAH	3	0.5	5.0	15.0	15124	3911	134.9	260.7
LSD	5%						1571		
	1%						2226		
	0.1%						3128		

The small difference from normal of rain and temperatures provided optimum conditions of capitalization of the foliar fertilizer, which resulted in significant yield increases in the tomato and vine crops. As a result of the application of the Folhum foliar fertilizer on the ADI 7 tomato hybrid in greenhouse with drip irrigation, the yield was of 17236 kg/ha, that is a 38.5% yield increase as compared to the nonfertilized control.

A Chasselas Doré variety vine culture was established for a 3 year period, i.e.

2008-2011, on a cambic chernozem soil at ICB Iasi, as a monofactorial experience in randomised blocks (Table 8).

The Folhum fertilizer was applied on the foliage in 3 treatments with a 0.5% concentration and in a quantity of 1000 l of diluted solution per hectare for each treatment.

As a result of the Folhum application, the grape yield increased by 3911 kg/ha in the fertilized variant as compared to the non-fertilized control, which represents a yield increase of 34.9%, i.e. 260 kg of grapes per 1 litre of foliar fertilizer.

CONCLUSION

The liquid fertilizer with humic acids produced high yield increases in the several crops in vegetation houses trials, i.e. 45.5% in the Dacia Pontica tomatoes and 49.2% in the Justin sunflower, as compared to the non-fertilized control.

In field trials, as a result of the application of Folhum the yield increase was 14.4% in sunflower with basic fertilization N_{80}, P_2O_5 80 kg/ha, as compared to the non-fertilized controls, and 34.9% in the grape vine plantation. The yield increase was 38.5% in the ADI 7 tomato hybrid grown in greenhouse with drip irrigation on a previously non-fertilized soil.

Based on such increases, the Folhum foliar fertilizer was licensed as RO-FERTILIZER, which means that it may be used in Romania (Interministerial Order no. 6/22/2004 as amended by Order no. 94 of 19 April 2010 published in the Official Journal of Romania no. 628 of 7 September 2010, for approval of the Regulations on the organization and operation of the Inter-ministerial Commission for authorization of fertilizers to be entered in the list of licensed fertilizers as RO-fertilizer, for use and trading in Romania).

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