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Interdigit dielectrometry of water vapour induced changes in granular starch

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ABSTRACT

Purpose: of this paper was a practical approval whether fringe field interdigit dielectrometry (FFID) can be useful for sensible monitoring of water molecules behavior within granular-starch-population sample during it's humidification process.

Design/methodology/approach: used was to design methodology and perform series of measurements involving calibration of a measuring system, sample preparation and to record initial stage of starch-granules-population samples humidification process as dielectric parameters response on the step of ambient atmosphere relative humidity (~0 to ~100%) at room temperature.

Findings: it was found that FFID enables to follow and isolate new features and characteristic stages of water vapors behavior during humidification of vacuum- dried starch granules population. The measurement of dielectric properties of freely stacked granules population with unperturbed inter-granular contacts areas differs from the one, during which this contacts are being broken.

Research limitations/implications: the possibility of new insight into humidification of micro-granular matter sample (starch granules population). It implies the necessity of collective (of global scale) model of dielectric properties creation. The evolution of dielectric permittivity is correlated with mass increase (water dipoles number) and adsorption rate as well as with absorption of water molecules within the granules population. Dielectric energy losses are correlated with evolution of interaction between water molecules and bio-polymeric matrix.

Practical implications: huge amounts starch granules are produced transported and stored so proper understanding of wheat response on humidity change is also of great practical importance.

Originality/value: of this paper relays on the fact that FFID was applied for the first time to starch granules population and it turned out to be effective tool in monitoring and modeling of dielectric properties of micro-granular matter population and for granular starch in particular. It is important in modeling of collective dielectric properties of this kind of matter as well as of practical reasons specified above.

Keywords: Biomaterials; Electrical properties; Granular matter; Starch; Humidification

MATERIALS

1. Introduction

Traditional dielectric spectroscopy is a method of measuring dielectric permitivity of samples placed in conventional parallel plates capacitor. In the case pf interdigir dielectrometry the flat capacitor, consisting of interdigitated comb electrodes is used (Fig.1). These electrodes are comprised of two interdigitated metal electrodes fixed on the flat surface of inert insulating substrate (e.g. quartz). The sample of investigated material is placed on this surface in intimate contact with the electrodes. One electrode is excited by with the sinusoidal voltage of fixed amplitude and frequency and the response measured (and recorded) as a value of resulting current together with phase difference between exciting voltage and current response. The electric fringing field penetrates the sample close to the sample – electrode interface. The depth of this penetration depends on electrodes width size and iterelectrodes distance [1-3]. One of the first interdigit dielectromety application was the cure monitoring of thermosetting resins and composites [4]. Recently, flat interdigit capacitors are used as humidity sensors [5], biosensors enabling fast and accurate detection of glucose, urea [6], and other bioreagent materials. One should expect, that this technique will become dominating in many disciplines of medical and biological applications [7]. The key advantage of the interdigit capacitor is the fact that every kind of interaction (electromagnetic radiation, reaction with chemical vapours and liquids) able to modify electric or dielectric properties of thin layer of sensing material placed on the iterdigit electrodes can be detected by means of measurement of ac-current response. This response should be specific and properly correlated with primary reason [8].

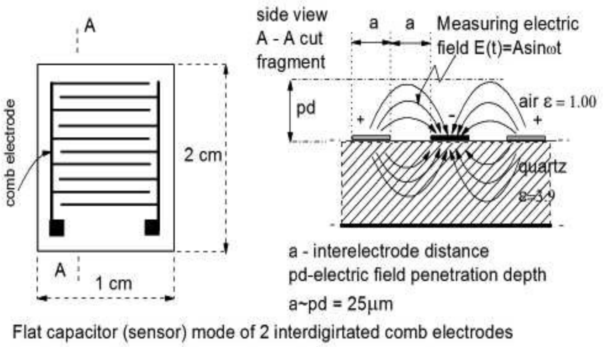

Fig. 1. The interdigitated – comb dielectric sensor geometry: front and side view cut of substrate and metallic electrodes

Biopolymers and biocompatible materials became recently subjects of many practical as well as technological investigations [9, 10].

Starch is the most abundant biopolymer created by plants and laid down in the form of granules. The size and shape of these granules differ with biological origin. Es biopolymer, starch is made of anhydroglucose units as mers linked by ∝(1.4)-glucosidic units. The granule structure is formed by two polymers: poly(1-4)∝-Dglucan, (amylose) which is linear polymer and the branched one called amylopectin connected through (1-6)∝ linkages. Amylopectin determines mainly the physical structure of starch granules by forming their crystalline component [11].

Starch biopolymers are very available source of renewable raw material for many practical applications. They are used in food industry, in pharmacy, paper industry and others. Electrical and dielectric properties of starch polymers were a subject of many investigations [12-14]. Molecular dynamics e.g. dielectric relaxations were isolated and identified as mainly local properties of polymeric chains involving local backbone or segmental motions [15] (β-relaxation). Motions of side groups of mers were assigned as γ-relaxation. These forms of molecular dynamics are rather similar for almost all kind of granular starches. This originates from local character of this dynamics which similar in some extend for all starches. The main source of discrepancies in theses investigations is tricky and complicated behaviour of water molecules (dipoles) and ions within starch granules structure (β_{wet}-relaxation). Water molecules can relatively easy penetrate granule's structure as well as the can leave them easy too.

Additionally, water presence increases dc-conductivity via ionic contribution. It is still uncertain how exactly relaxation and conductivity processes are correlated with swelling, gelatinisation, reversing swelling and retro gradation of starch.

The physical structure of starch granules has ability of birefringence. Polarized and laser light can be applied to observe many interesting effects [16]. Some of them may have a potential of practical application [17] Water binding capacity and water vapour adsorption isotherms for native and modified starches were a subject of many investigations [18, 19]. Water sorption ability of granular starch originates from interactions of water molecules with free hydroxyl groups of the glucose units. Another way of water sorption description is to consider two steps process: primary adsorption sites with enhanced binding ability (hydroxyl groups) and secondary step in the form of capillary wetting. Determination of mixed character of water sorption is very difficult to perform in the terms of adsorption isotherms models.

Considering all above mentioned properties of starch one can ask another question: what about to treat a free stacked starch granules sample as micro-granular matter form and expose it to water vapour and monitor changes of dielectric and electric properties by means of interdigit dielectrometry in statu-nascendi? Attempt to answer this question was the aim of this work. In practice it means that one is going to look for correlations between changes of dielectric and electric properties induced by water-vapour sorption and other processes involved but within the scale of observation of much more than one granule structure. One can consider it as global approach or micro-granular matter model.

2. Experimental approach and methodlogy

2.1. Measurement of size distribution of investigated starches

The starch granules portion was placed on the microscopic glass. The drop of immersion fluid (n=1.5) was put and covering glass pressed carefully on the top. Next, such a sample was placed on the optical microscope table (Biolar polarizing-interference PZO Poland). Starch granules were identified in the polarized light and photographs were taken by means of CCD Delta Pix camera equipped with Delta Pix program enabling linear size calibration for each magnification used. Next, sizes of granules were collected and histograms of granules diameters were prepared. The parameters of distribution were calculated as: a max and min diameters in μm, and mean size also. Some starches have unimodal, others bimodal granules sizes distribution.

2.2. Starch samples preparation for humidification monitoring

Every starch sample was dried in the in vacuum (10^{-2}Tr) and 50^{0}C temperature for 2h. Next, using special calibrated vessel

(7.7±0.05mm^3) was applied to take two samples of dried starch: one was placed within chamber with saturated water vapour and stabilized temperature 23^{0}C and precise torsion balance for monitoring of mass increase in time as a response on humidity step to ~100%RH. The second portion of the sample of the same volume was placed within specially designed measuring chamber equipped with Peltier-type heat pump, PT-100 temperature sensor and independent measurement of atmosphere temperature and RH%. The calibrated volume portion of dry starch sample was distributed on interdigit sensor of Ms25μm type. Thus, the layer of dry starch about 0.5mm thick was covering the active surface of the sensor. Measuring chamber was hermetically closed and distilled water was introduced on it's bottom in order to create the rapid increase of relative humidity to saturated value (~100%). The temperature of interdigit sensor (and starch sample was stabilized at 23^{0}C by RE15 Lumel microprocessor temperature regulator with PC program Lumel-Regulacja. Immediately, the program WinDETA (Novocontrol Germany) was started and by means of Agilent 4284A precise RLC meter, dielectric and electric parameters were measured and recorded. The measurement was running for about 5*10^{5}s. This value of time was selected in order to prevent irreversible granules structure changes. It corresponds to about 25 to 30% sample mass increase (by weight).

2.2. Effective dielectric and electric properties of starch exposed to water vapour

The details of measurement geometry of the sample- interdigit electrodes are presented in Fig. 2 and Fig. 3. The measuring field is penetrating the population of granules and

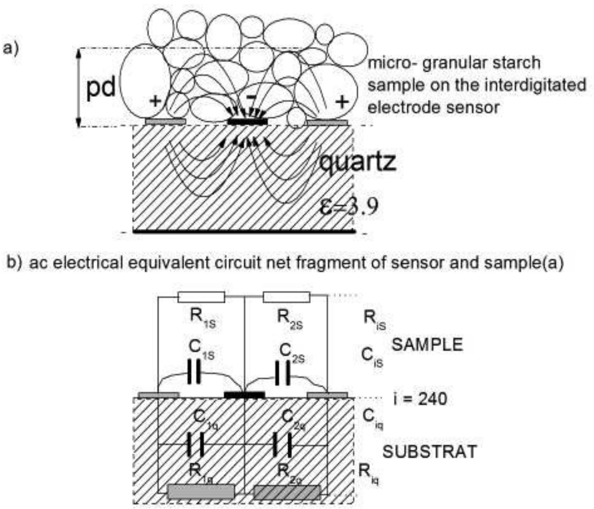

Fig. 2. a) micro – granular matter (starch) sample on the interdigitated electrode sensor, b) ac – electrical equivalent circuit – net fragment of sensor (substrate) and micro – granular sample placed on the sensor surface

Agilent 4284A meter is measuring parallel equivalent complex impedance Z_M^* (Fig.3) as a function of frequency and amplitude of sinusoidal measuring voltage et constant temperature and atmosphere humidity (RH%) within the measuring chamber. The computer program is calculating the effective complex impedance of the sample Z_S^*. Others dielectric properties of investigated sample as: ε^*- the complex effective dielectric permittivity, M^*- the complex effective dielectric modulus, admittance Y^*, conductivity σ^*, phase angle, are calculated also automatically.

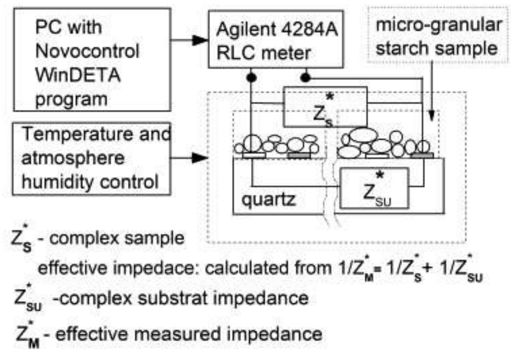

Fig. 3. The effective complex impedance measurement principle and scheme for micro – granular matter (starch) placed on the interdigitated electrode sensor

3. Measurements outcomes and interpretation

3.1. Geometry of starch granules population

Distribution of maize-starch- granules population diameter taken from microscopic investigation is shown in the Fig.4.

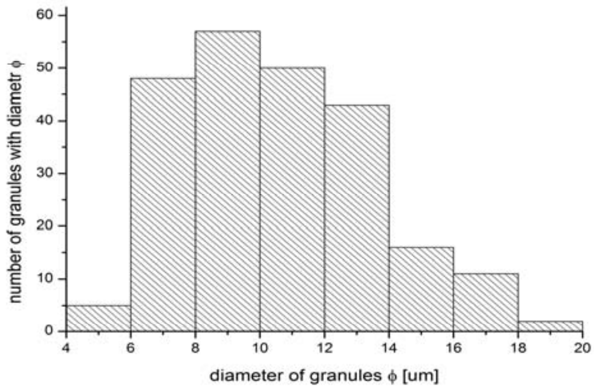

Fig. 4. Maize starch granules diameters distribution

The most abundant diameter within investigated granules population in the range (8 ÷ 10) μm, (maximum of the distribution). The whole distribution is unimodal (single maximum) and asymmetrical (Fig.4) with half – width value about 8μm. The defected granules were not observed in investigated sample.

3.2. Outcomes of real time dielectric monitoring of maize starch humidification process

The time and frequency dependence of dielectric permitivity (Eps') for granular maize starch is presented in the Fig. 5.

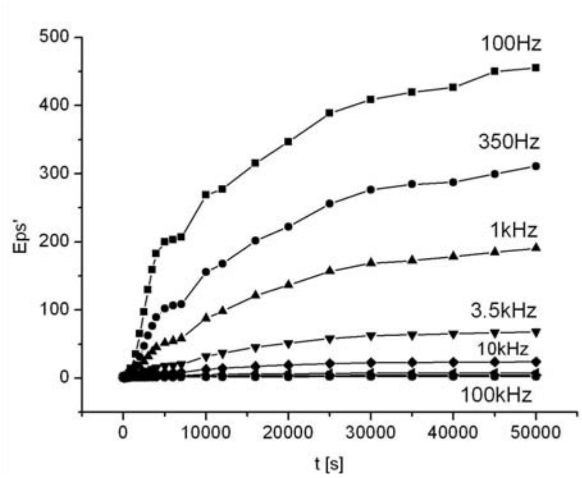

Fig. 5. The effective dielectric permitivity (Eps') of maize-starch-granules sample as a function of time for 9 selected frequencies. It was measured as the response on the step of ambient atmosphere relative humidity (RH) from 0 to ~100% at room temperature. The RH step was initiated for t=0s

Dielectric monitoring of step RH - (Eps') time response was continuing up to 50000s. It represents an initial period of water vapours uptake by maize starch granules. It involves a substitution of dry air by water vapour (wv) saturated one, adsorption of wv on granules surfaces, migration of wv and water molecules (wm) into sticking areas between granules, partial dissociation of adsorbed wm, absorption of wm into granules interiors and capilong water condensation. The total water uptake during 0 ÷ 50000s time of monitoring, was less than ~27% by weight. It is known, that such on water uptake is of reversible character and does not change irreversibly the physical organisation of starch polymers in graules. The capilary condensation of water vapours are able to induce amylopectin crystalline lamelles line up into smectic like layers. Proces of (Eps') value increase was demonstrated in linear scales (Fig.5) in order to show proportions between all processes involved in the global scale. Additional details of very initial period of time (t<7000s; Fig.5) can be resolved in log-log scale. This will be a subject of further analysis. During the whole monitoring time used, (Eps') value undergoes increase from ~2 to ~450 value. This increase is strongly frequency dependent. For frequencies down from 1kHz, the interdigit dielectrometry turned out to be very selective way of following the humiditifieing process of granular starch. Independently of frequency one can isolate ~5 processes (Fig.5) synchronized in time. Generally, changes of (Eps') value can be treated as reflecting an increase of dipoles number in the polymeric matrix (granule structure) and changes of their polarizability. Dipoles (wm) number total value can be estimated from mass increase monitoring in time. Changes if polarizability originate from physical and chemical interactions of wm entering the inter-granular space, granular surfaces and intergranular contact areas. Both above mentioned kind of changes are able to manifest themselfs as contributions to total polarization of granules system/net involving ~1500 ÷ 2000 pices. Colected data will be used to construction of dielectric properties model for micro-granular mater. The energy loss factor (tanδ) for maize starch granules population, measured as a response on relative humidity step (0 ÷ ~100%) at room temperature is presented in the Fig.6. The frequency dependence of tanδ monitored in time is also presented there.

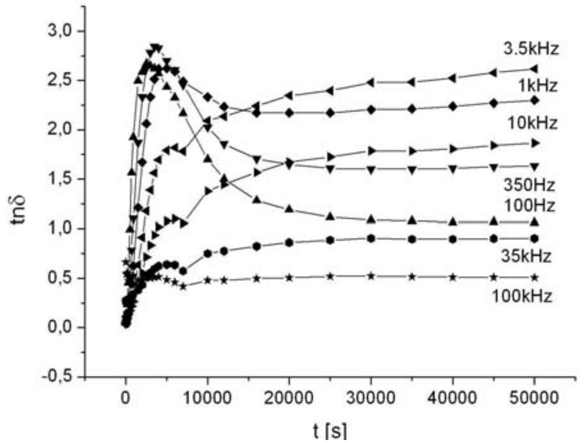

Fig. 6. The effective energy loss factor of maize-starch granules population as a function of time for 7 selected frequencies. It was measured as the response on the step of ambient atmosphere (0 ÷ ~100%) relative humidity at about t≈0s

The initial process of wv uptake (up to ~7000s) is correlated with similar behaviour for (Eps') in time. During the whole time of dielectric monitoring tanδ values undergous a rapid increase from values of ~10^{-2} (dry starch is a dielectric) up to ~2.7 at about 5000s and a transient minimum values for all frequencies used correlated with transient slowing of (Eps') increase at ~7000s. For Eps'(t) the frequency dependence got monotonical character: the highest values were observed for the lower frequency applied. General feature of Eps'(t) record is increase with time and stronger tendency to saturation for higher frequencies. Thus, the Eps'(t) behaviour reflexes the increase of water content. In the case of energy losses (Fig.6) the frequency dependence got quite diffrent character. During the initial process (up to ~7000s), tanδ values are fast increasing for frequencies up to ~1kHz with subsiquent also fast decrease to relatively constant values (100Hz, 350Hz and 1kHz). For frequencies f≥3.5kHz, initial transient peaks value (at ~5000s) are aproximately inversly proportional to frequency values but with tendency of following further increase. Again, the initial process details will be analysed in the log-log scale within the time range up to ~7000s. As it can be seen in the

Fig.6, interdigit dielectrometry can be treated as sensitive tool enabling for monitoring in real time the energy losses changes taking place during wm uptake from saturated water vapour in room temperature. Energy losses measure in the form of tanδ values reflexes losses originating from ac conductivity (water disociation and residual ions in granules interiors) as well as partial cpnversion of rotating dipols energy (under the external electric field action) into a heat (relaxation). The frequency dependence of tanδ values evolution in time should be treated as potential information source about evolution of water dipols mobility, physical and chemical bouding interaction, leading to differencies in water dipoles immobilization. Another way to monitore humidification of starch granules population is to record complex impedance values as a function of time and frequency. Outcomes of impedance measurements taken for the same process as above, for maize starch granules population are presented in the Fig.7.

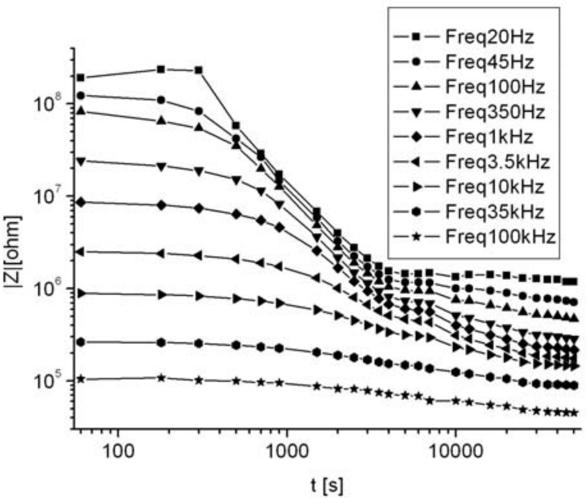

Fig. 7. The absolute value of electric efective impedance ($|Z^*|$) evolution measured as response on the step of ambient atmosphere relative humidity step (0 ÷ ~100%) at room temperature

The initial impedance values, for dry starch depends strongly on frequency and obeys more than 3 orders of magnitude step (10^5 ÷ 10^8)Ω. Water vapor uptake occuring during first ~5000s reduces the upper impedance value to ~10^6Ω. For all frequencies used the impedance is falling down along water uptake advance. The highest selectivity of $|Z^*|$ changes occure for low frequencies (down from ~3.5kHz). The break-point observed formarely at ~7000s is also present (Fig.7). Wet maize starch granules population (t~5000s) get the frequency dependence of impedance values within reduced range (~$5{\cdot}10^5$ ÷ ~$2{\cdot}10^6$)Ω. The character of $|Z^*$(frequency)$|$ dependence undergoes systematic evolution and will be a mater of further investigation and modeling. The same experimental data can be analysed as real Z' and imaginary Z'' components of complex effective microgranular matterimpedance giving insight into the equivalent circuits parameters evolution during water uptake by the starch population granules. The time evolution of effective phase angle (Phi[deg]) for maize starch granules population, measured during water uptake as described formerly is shown in the Fig. 8.

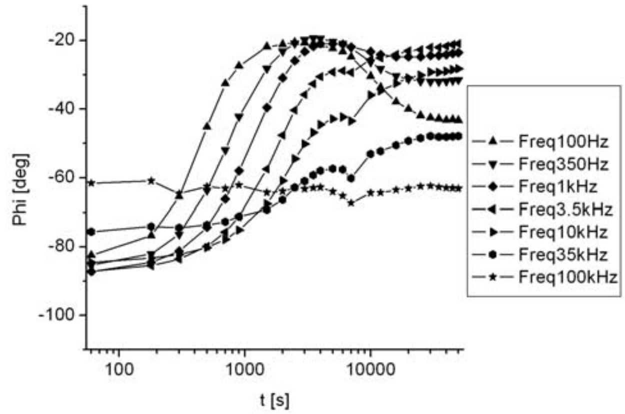

Fig. 8. Time and frequency dependence of effective phase angle (Phi[deg]) for maize starch granules population measured as response on ambient atmosphere relative humidity step 0 ÷ ~100% at room temperature

Phase angle reflexes changes of the angle between measuring voltage applied to the interdigit sensor with microgranular matter sample (here the maize – starch) and resulting current. It is presented in log scale of time in order to give insight into details of initial process of wm uptake by the population of starch granules. Again, the discontinuity for for t~7000s is present for all frequencies. Systematic changes are visible with time and frequencies dependencies. For t<~7000s and below 10kHz initial evolution of Phi values undergoes systematic shift in time with the order of increasing frequency values. For frequencies higher than ~3.5kHz this dependence vanishes and for t>~7000s further evolution of Phi values is similar to thouse of tanδ (Fig.6). The weeker time dependence takes place for 100kHz (Fig.8). Initial values of Phi for low frequencies are gathered around ~85deg vale (dielectric isolator values). During ~(0 ÷ 5000)s the Phi value decreases to ~20deg like for semiconductors. Thus one can postulated that during exposition on saturated water vapour, at room temperature, freely stocked microgranular sample population of maize starch undergoes the isolator – semiconductor transition. This transition observed in-statu-nascendi seems to be reported for the first time. It should be treated as cplective dielectric property of microgranular matter population property. It was not reported yet because of the technic used. It is in comon to keep starch sample in the chamber with controled atmosphere humidity expose the sample on wv and to take sample, place it within measuring capacitor to measure dielectric permitivity change. During this operation the structure and distribution of water in contact areas are disturbed and above described colective dielectric properties could not be observed.

4. Conclusions

The interdigit dielectrometry applaying flat interdigitated sensor turned out to be effective and quite selective method of monitoring the process of humidification of micro-granular matter maize starch granules population. Freely stocked granular sample can be easy exposed on water vapour and population of ~(1500 ÷ 2000) granules are within the penetration depth of measuring electric field. PC-control and automatic measurement involves a calibration of the sensor used. This in turn enables programed measurement of intensive and extensive dielectric properties of micro-granular matter samples placed on the flat interdigitated sensor. The measurements of effective dielectric permitivity Eps', energy loss factor (tanδ), effective complex impedance (Z^*) as well as phase angle (Phi) as a functions of frequency ~(20Hz ÷ 100kHz) and exposition on water vapours time gave a new insight into a mechanisms of water vapour molecules behaviour in population of starch granules. Outcomes of measurement enables to analyse processes involved in initial stage as well as further secondary ones. Colected data in time and frequency should be treated as positive verification of selected methodology and will be used to construct model of effective dielectric properties evolution taking place during the transition from dielectric to semiconductor state of freely stocked micro-granular maizy starch population sample. New method of observing of water behaviour in granular starch is also of practical importance becouse starch is one of very abundant biopolymer applied in pharmacological and food industry. The potential correlation of recorded dielectric changes with total water uptake speed monitored in time for the same sample should be useful in modeling of microgranular matter dielectric properties treated as colective ones. The possibility of calenloting dielectric modulus values as well as ac-conductivity ones may be even more sensitive for changes of water behaviour.The same technique can be applied for monitoring of drying processes of granular starches of different origin or chemicaly/physicaly modified ones.

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