DRYING KINETICS

Abstract

The three fundamental techniques for drying food include surface diffusion on pore surfaces, liquid or vapor diffusion resulting from changes in moisture content, and capillary action induced by surface forces in granular and porous food products. The thin-layer drying process of food products is significantly influenced by various variables, including drying time, temperature, relative air humidity, air flow rate, surface area, material thickness, volume, and local or partial pressure. Among these are the material thickness (size) and drying temperature, which have the most effects on fruit and vegetable drying. Numerous models are referenced in the literature for examining the drying of food materials. Methods of thin layer drying includes theoretical, semi-theoretical and empirical. However, most commonly employed categories are semi-theoretical and empirical thin-layer models. Using optimization techniques, optimal models for drying agricultural products in thin layers can be predicted.

Keywords: Drying kinetics, Techniques, thin layers, Mathematical models

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I. INTRODUCTION

Food is one of the most basic human necessities, but every year, about 1.3 billion tonnes of food are lost owing to unfavourable weather, pest infestations, early harvesting, processing issues, overproduction, unstable markets, and inadequate handling and storage facilities [1]. Therefore, food processing and storage are practical ways to lower these losses, fight hunger, and advance global food security. Food is therefore regarded as the drying object. A substantial amount of moisture is removed from agricultural products and foodstuffs during drying in order to prevent or reduce microbial or enzymatic reactions and preserve the optimum level of nutrients [2].

Drying is among the earliest and enduring methods of food preservation. It remains a vital technique for preserving food. Dried foods have extended shelf lives, reduced size and weight for easier handling during transportation, become free-flowing solids, and maintain the desired quality. This preservation technique is effective because many enzymes responsible for undesirable chemical changes in food require water to function, and bacteria contributing to food spoilage and decay cannot thrive or reproduce without sufficient water.

Drying is typically done outside in the open sun (OS). Despite the ease and low cost of drying in OS, this method is ineffective since it requires a wider drying surface and a longer dwell time. Additionally, due to contamination from dust and moisture in the air, dried goods produced in an open setting will be of very poor quality [3]. Three categories apply to drying procedures:

Drying by air and contact with atmospheric pressure. Heat is transferred through the meal during air and touch drying, whether from heated surfaces or hot air. The water vapor is removed using the air.

- Drying by vacuum. The faster rate of water evaporation at lower pressures compared to higher pressures is utilized in vacuum drying. Although radiation can also be used, conduction is the usual method of heat transmission in vacuum drying.
- In the freezer. Food that has been freeze-dried allows water vapor to escape from it. The food structure is better kept in these conditions. To guarantee that sublimation takes place, the dryer must be set to the proper temperatures and pressures.

In industrial drying processes, heat is administered to food products within a closed system through either direct or indirect methods, contingent on the heat source. Direct drying involves the transfer of heat between the product and the drying medium through convection, while indirect drying employs a physical barrier, and heat is transmitted through conduction. Certain applications utilize radiation, such as microwave or radio frequency drying, where heat is transferred through the radiation mode. Among these methods, direct convective drying, which employs hot air or direct combustion gases as the drying medium, is the most widely utilized [4]. Various drying techniques, including air drying, sun drying, spray drying, drum drying, and freeze drying, are employed to reduce moisture content [5, 6, 7, 8]. Dried foods typically refer to those from which water has been removed, necessitating the provision of latent heat of vaporization to evaporate the water present in the food. Consequently, the drying unit operation is influenced by two critical process-controlling factors:

- Heat transfer to produce the vaporization's required latent heat,
- Water separation from food is achieved by the passage of water or water vapor through the food substance and then out of it.

Aonla is a seasonal fruit, thus processing is needed to make it available all year round and extend its shelf life [9]. It is typical practice to increase shelf life by reducing water activity since it inhibits microbial growth in fruits and vegetables. Fruits and vegetables' physical-chemical, nutritional, and qualitative characteristics, such as color, texture, and flavor, may change while drying [10].

Mathematical Models: The kinetics of heat and mass transport are significant in the drying process. Mathematical equations serve to elucidate the behavior of the drying process, offering advantages in terms of cost and time savings [11,12]. Key factors affecting the mass transfer rate during drying encompass temperature, relative humidity, air flow rate, thickness, and shape of fruits and vegetables. Kinetic models play a pivotal role in optimizing the drying process to minimize energy consumption, equipment stress, and enhance product quality [13, 14, 15]. Drying kinetics involve the formulation of mathematical equations that represent typical behaviors and facilitate the optimization of drying properties. Mathematical models used to depict drying processes are inherently complex, as they consider the concurrent unsteady transfers of momentum, heat, and mass. These models also account for the physical transformations experienced by drying objects, including alterations in volume, crystallization, or glass transitions. Additionally, they involve the integration of the most suitable energy source. Therefore, drying is not merely a procedure for eliminating moisture but rather a fusion of science, which entails understanding thermodynamics, transport properties, and material science; technology, involving process design, optimization, energy integration, and control; and art, encompassing extensive experimental observations and operator experience.

II. MECHANISM OF DRYING

The three fundamental techniques for drying food include surface diffusion on pore surfaces, liquid or vapor diffusion resulting from changes in moisture content, and capillary action induced by surface forces in granular and porous food products [16]. Hygroscopic materials typically undergo drying at a consistent pace, progressing through phases of decreasing rate until they reach equilibrium. The initial falling rate period begins when the surface layer of solids or particles appears to have dried, reducing the moisture content to its critical level. Unlike the constant rate phases, falling rate stages are primarily governed by liquid diffusion resulting from changes in moisture concentration and internal product conditions. Internal variables such as moisture content, temperature, and product structure are crucial during these decreasing rate periods. Vapor diffusion is involved in the subsequent falling-rate drying phases, influenced by changes in moisture content and internal product conditions [19] [20]. It is widely acknowledged that the drying process of biological products, especially during the falling rate phase, is predominantly governed by liquid and/or vapor diffusion mechanisms [19] [21]. Capillary and liquid diffusion theories are most commonly applicable to drying food items [22]. Diffusion, contingent on the moisture content of the samples, serves as the predominant physical mechanism governing moisture transport within the material [23] [24] [25]. Moisture contents are more conveniently expressed on a dry basis to facilitate modeling [27] [28]. Figure 1 provides insight into the drying rate and temperature variations over time, allowing the identification of the optimal drying method for a product. Typically, during the initial drying phase, the equilibrium air temperature surpasses the product temperature [29]. As a result, the drying rate between points A and B increases with the rising product temperature until the surface temperature reaches equilibrium, corresponding to lines B to C.

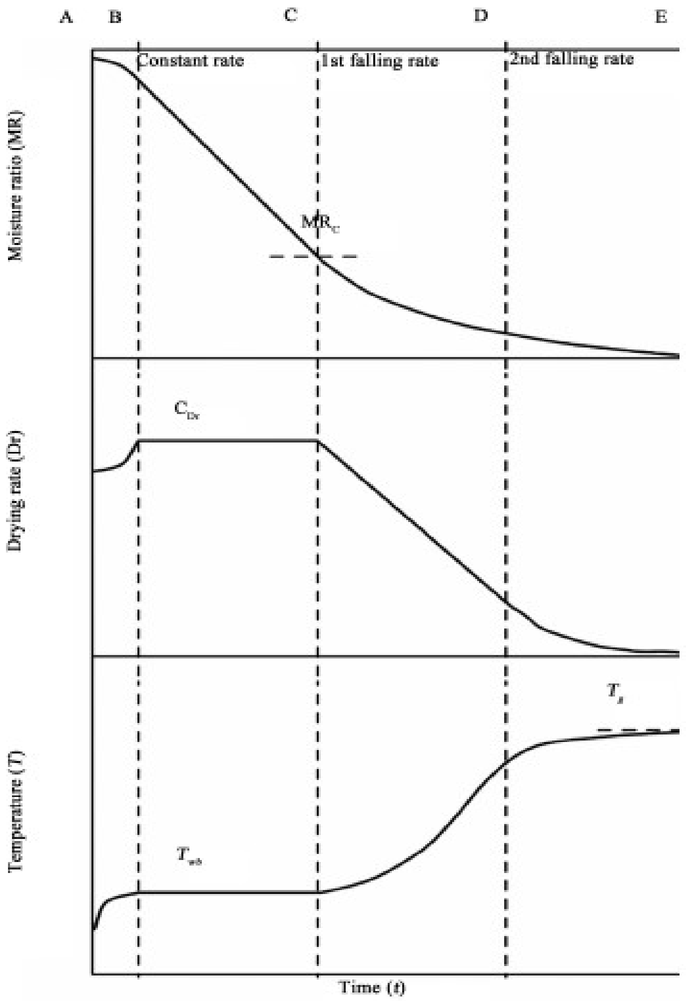

Figure 1: Typical agricultural product drying curve with periods of declining and constant rates [31].

Characterizing the drying process for biological and agricultural commodities commonly involves recognizing multiple stages occurring under constant conditions. Following the initial constant rate period (from point B to point C), marked by the evaporation of pure water, one or more falling rate periods ensue. In these periods, moisture movement is influenced by a combination of external-internal resistances or external/internal resistance to heat and mass transfer [30]. The falling rate phases are significant for many fruits and vegetables, as drying is primarily controlled by a diffusion process. Typically, drying concludes upon reaching steady-state equilibrium. It is noteworthy that the physical properties of the product, particularly its surface, undergo changes during the constant rate phase.

This phase is predominantly governed by the forces of gravity and capillary action. Throughout this stage of the drying process, multiple factors, such as temperature, drying air velocity, and relative humidity, exert an influence on the product. The commencement of the first decreasing rate phase (from point C to point D) occurs as the product's surface coating dries, and the moisture content reaches its critical moisture level. Subsequently, the material transitions from the first falling rate phase to the second falling rate period (from point D to point E) as the drying process advances [31].

Numerous models, encompassing theoretical, empirical, and semi-empirical categories, are referenced in the literature [21] [32] for examining the drying of hygroscopic materials. Nevertheless, the most commonly employed categories are semi-theoretical and empirical thin-layer models [29] [33] [34] [35].

III. KINETICS OF DRYING

In the realm of food processing, the kinetic modeling of process parameters proves highly beneficial. The primary processes encompass physical and (bio)chemical reactions, unfolding with distinct kinetics and at specific rates. The ability to statistically quantify these changes and their rates is facilitated by kinetic modeling. This robust tool serves to unravel fundamental reaction mechanisms, proving essential for quality modeling and quality control, necessitating a comprehensive understanding of the underlying mechanisms [36].

Understanding of thermodynamics and kinetics is necessary to comprehend the progression of reactions. The driving force and the barrier to change combine to determine how quickly a reaction moves forward. Thus, there is a close connection between kinetics and thermodynamics [6]. Thus, choosing appropriate drying methods and controlling the drying processes will be made easier with an understanding of drying kinetics. It is also essential for engineering and process improvement. Determining the optimal drying conditions through a full-scale experiment can be expensive.

Hence, the utilization of drying kinetics is essential for characterizing the moisture removal process and its correlation with the process factors. Therefore, a comprehensive understanding of the drying rate is crucial when formulating a drying model. [37].

Despite the fundamental nature of kinetics, modeling the drying of particles or thin layers of materials is crucial for gaining an understanding of the underlying transport mechanisms. It is also a prerequisite for effectively simulating and scaling up the entire process when optimizing or controlling operational parameters. Simple models with a clear physical interpretation are valuable for engineering purposes. The design, development, and optimization of dryers all necessitate the mathematical modeling of the dehydration process [38]. This process primarily involves a comprehensive examination of drying kinetics, elucidating the mechanisms at play, and considering the impact of various process factors on moisture transfer [39]. In simpler terms, it serves as a tool for analyzing drying kinetics, investigating drying variables, and enhancing drying conditions and parameters [40] [41].

Factors affecting Kinetics of Drying: The drying process of food products, such as fruits and vegetables, is significantly influenced by various variables, including drying time, temperature, relative air humidity, air flow rate (or velocity), surface area, size (material thickness), volume, and local or partial pressure. [42].

Among these are the material thickness (size) and drying temperature, which have the most effects on fruit and vegetable drying [43] [44] [45]. Cerquera et al. [46] thus identified the factors that had the most effects as air speed, final moisture content, product contraction or shrinkage, and attributes pertaining to food quality and preservation.

The results demonstrated that among the factors affecting thin-layer drying kinetics of fruits and vegetables, temperature and thickness exerted the greatest influence, while air velocity and relative humidity had a comparatively lower impact [47]. In contrast, Gacula and Singh [48] presented evidence suggesting that temperature has a more significant effect on the drying constant than thickness. Although the interactions between temperature and thickness did not substantially alter the value of the drying constant, these conclusions aligned with the observations of potato researcher Wang [49].

IV. THIN LAYER DRYING PROCESS

A thin layer is defined by a minimal product thickness, allowing for the assumption that air properties remain constant and uniform throughout the layer. The thin-layer drying process involves drying individual grains or material particles fully exposed to the drying air. Typically, the drying process is divided into two phases: the falling drying rate and the constant drying rate [50].

During the constant rate drying phase, the material contains a significant amount of water, resulting in the presence of liquid surfaces that behave somewhat like an open body of water during the drying process. The drying rate is primarily dictated by the interaction between the liquid water and its surrounding environment, rather than by the solid material itself. Substances that exhibit an initial constant rate of drying encompass wet sand, soil, pigments, and washed seeds. The energy needed for drying is generated through radiation, conduction, or convection mechanisms.

In practical situations, agricultural food products undergo the drying process with decreasing drying rates. The falling rate period is characterized by the equilibrium moisture content, forming a curve ranging from nearly 0% to almost 100% relative humidity. The falling rate phase involves two primary processes: the migration of moisture from the material's interior to its surface and the subsequent removal of moisture from the surface. Thin-layer drying can also be defined as the drying of a single layer of sample particles or slices exposed to a batch of drying air with suitable physical qualities. The process of evaporatively removing moisture from a porous media is called "thin-layer drying." Another term for it is "passing excess drying air through a thin layer of material until the equilibrium moisture content is reached" [52, 53].

1. **Theoretical Method:** When assessing the external resistance to moisture transfer between air and the product, the other two criteria come into consideration. The internal barrier to moisture transfer, however, is the sole focus of theoretical models. These

models are grounded in Fick's second law of diffusion, as proposed by Fick. On the other hand, semi-theoretical models often stem from Newton's law of cooling and various adaptations of Fick's second law. Fick's second law of diffusion serves as the most widely used theoretical framework. Nevertheless, theoretical models can be overly intricate for practical applications, are often inadequate, and may yield inaccurate results. Their applicability in dryer design is limited due to the numerous assumptions they rely on, resulting in significant inaccuracies. While a theoretical equation provides a more comprehensive understanding of the transport processes, an empirical equation closely aligns with experimental data without requiring knowledge of the underlying transport mechanisms.

When evaluating the external resistance to moisture transfer between air and the product, the other two criteria are considered. The internal barrier to moisture transfer, however, is the exclusive focus of theoretical models. These models are based on Fick's second law of diffusion, as proposed by Fick. Semi-theoretical models, on the other hand, often derive from Newton's law of cooling and various modifications of Fick's second law. Fick's second law of diffusion serves as the most widely used theoretical framework. Nevertheless, theoretical models can be excessively intricate for practical applications, are frequently insufficient, and may yield inaccurate results. Their utility in dryer design is constrained due to the numerous assumptions they rely on, leading to notable inaccuracies. While a theoretical equation provides a more comprehensive understanding of the transport processes, an empirical equation closely aligns with experimental data without requiring knowledge of the underlying transport mechanisms.

2. **Semi-Theoretical Method:** To enhance usability and better align with the drying data of the food product being processed, semi-theoretical models have been developed. The development of semi-theoretical models has been a focal point in striving for a balance between theoretical foundations and practical applicability. These models frequently employ mass transfer principles in conjunction with Newton's Law of Cooling. This equation assumes an isothermal environment and considers only the product's surface as the source of resistance to moisture transfer. The streamlined generalized series solutions of Fick's second law are characteristic of semi-theoretical models. However, these models are effective only within certain parameter ranges, including temperature, relative humidity, air velocity, and moisture content. Semi-theoretical models require less computational time and do not account for the specific form of the dried material. Examples of semi-theoretical models include the two-term models of Henderson and Pabis, Lewis, Page, and Modified Page.

3. **Empirical Method:** The empirical method, based on experimental data and dimensionless analysis, is a technique employed in drying studies. Empirical drying models are built on the concept of a direct relationship between drying time and average moisture content. This method proves valuable for illustrating drying curves under specific experimental conditions but neglects the fundamental principles of the drying process. The parameters in empirical models lack physical significance, posing a challenge in providing an accurate representation of the underlying processes during drying phenomena. Empirical models are most effective at describing drying curves for particular drying conditions, focusing on the trends within dependent and independent experimental/process variables. However, they do have limitations, relying heavily on

experimental data and offering limited insights into the intricate details of heat and mass transfer during drying processes.

V. THIN LAYER MODELS

Understanding the patterns displayed by dependent and independent experimental/process variables depends heavily on empirical models. The primary shortcomings of empirical models, however, are their heavy reliance on experimental data and their inadequate treatment of heat and mass transfer details during the drying process [16]. These models assume constant diffusivity and necessitate a constant product temperature, as indicated in the model requirements [54] [63].

Henderson and Pabis model is a particular instance of the Lewis model. Bruce [56] claims that the model is flawed because it exaggerates the first period of drying while underestimating the last period.

Drying kinetics models do not account for the interaction of components beyond drying time. The intricate non-linear relationship between the kinetics of drying and associated factors makes it impractical to develop comprehensive variable models on a large scale, despite the absence of such models currently [64]. The introduction of thin-layer drying models to elucidate drying behavior was initially proposed by Lewis [65]. Lewis formulated a semi-theoretical model, akin to Newton's law of cooling, for porous hygroscopic materials. The subsequent model was established.

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(-kt) \qquad (1)$$

Where MR is moisture ratio, k is drying constant (m^{-1}), t is drying time, X ,X_e , X_o are moisture content at any time, equilibrium and initial, respectively.Page [66] modified the Lewis model by adding a dimensionless empirical constant(n) and used it for study the drying behaviour of shelled corns.

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(-kt^n) \qquad (2)$$

Overhults et al. [67] adapted the Page model to investigate the drying kinetics of soybeans, and the resultant equation is as follows (this model is known as ModifiedPage-I Model)

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(-kt)^n \qquad (3)$$

Furthermore, a minor modification to (3) is made to explain the drying kinetics of soybeans (this model is called the Modified Page-II Model).

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(\,(-kt)^n) \qquad (4)$$

Additionally, Diamante and Munro [68] altered the Page model for sweet potato drying and suggested the following equation (this model is known as Modified Page Equation (2) Model)

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(-\mathrm{k}(\mathrm{t}/\mathrm{l}^2)^{\mathrm{n}}) \qquad (5)$$

Where l is a dimensionless empirical constant. Apple and potato drying behaviors can be described by semi-theoretical thin-layer drying models since the drying process is thought of as the exterior resistance to moisture transfer between air and product. Experimental data for apples and potatoes selected from the literature were used to test the aforementioned models. These models fall short of accurately describing how apples and potatoes dried in the last drying hours. In order to better understand the drying kinetics of apples and potatoes in this setting, we added a linear element to the Lewis model.

$$MR = \frac{X-X_e}{X_o-X_e} = \exp(-kt) - akt \qquad (6)$$

Where k is the drying constant (m^{-1}) and an is the dimensionless adjusting model constant that was added to get the greatest possible model fit to the experimental data. The drying circumstances, temperature, air velocity, humidity, and drying techniques all affect the drying constant, k. The moisture ratio (MR) can be calculatedby (7) instead of $\frac{X-X_e}{X_o-X_e}$due to the small value of X_e , as compare to X , and X_o [69].

$$MR = \frac{X}{X_o} \qquad (7)$$

Therefore, (6) reduced to

$$MR = \frac{X}{X_o} = \exp(-kt) - akt \qquad (8)$$

As can be observed in the literature [29], these models are just variations of one another, using the Newton (Lewis) or Page models as their foundation. It is done to make up for one another's flaws. It has been discovered that the models accurately depict the drying kinetics of various fruits and vegetables. Dimensionless (model) constants (a, b, c, d, l, α) and drying constants (k, g, h, K_1, K_2, K_o) are specific to each equation.

The mathematical models applied to the thin layer drying curves of different agricultural products are displayed in Table 1 below.

Table 1

Model Name	Model	Reference
Page	MR= $\exp(-kt^n)$	[66]
Newton	MR= $\exp(-kt)$	[70]
Logarithmic	MR=a $\exp(-kt)+ c$	[71]
Modified Page	MR= $\exp[(-kt^n)]$	[72]
Modified Page II	MR= $\exp[-k(\frac{t}{l^2})^n]$	[73, 74]
Handerson and Pabis	MR=a $\exp(-kt)$	[75]
Modified Handerson and Pabis	MR=a $\exp(-kt) + b \exp(-gt) + c \exp(-ht)$	[76]
Two Term	MR=a $\exp(-k_o t) + b \exp(-k_1 t)$	[77]
Thompson	$t = a \ln(MR) + b[\ln(MR)]^2$	[78]
Combined Two term and Page	MR= $a \exp(-kt^n) + b \exp(-ht^n)$	[79]

VI. STATISTICAL EVALUATION/GOODNESS OF FIT STATISTICS

Statistical measures are utilized for the evaluation and comparison of different thin-layer drying models. Various statistical metrics are employed to gauge the quality of the fitted models, including Sum Square Error (SSE), Mean Relative Deviation (E%), Reduced Chi-Square ($\chi 2$), Root Mean Square Error (RMSE), and correlation and determination coefficients (R^2), among others. When using metrics such as the correlation coefficient or coefficient of determination, the model with the highest R^2 value is selected to represent the drying curves, and the same criterion applies to other statistical measures. Therefore, a model is considered to have a good fit if it exhibits a high R^2 value and low values for other parameters, such as $\chi 2$, RMSE, E%, and SSE [27, 80, 81, 82, 83]. Alternatively, a nonlinear least squares method based on the Levenberg-Marquardt algorithm can be employed to fit experimental data to specific equations. The coefficient of determination plays a crucial role in selecting the optimal model, serving as a means to validate the linear relationship between experimental and model-calculated data [84].

The number of constants does not, however, affect the choice of the best model for characterizing the drying behavior of fruits and vegetables. Instead, it is based on a number of statistical measures. According to literature, statistical indicators have frequently been employed to choose the best drying models [85, 86, 87, 88].

$$RMSE = \sqrt{\sum_{i=1}^{N} \frac{\left(MR_{Experimental\ value} - MR_{Predicted\ value}\right)^2}{N}}$$

$$E\ (\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{Experimental\ value - Predicted\ value}{Experimental\ vlaue} \right|$$

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(MR_{Experimental\ value} - MR_{Predicted\ value}\right)^2}{(N-n)}$$

$$SSE = \frac{1}{N}\sum_{i=1}^{N}\left(MR_{Experimental\ value} - MR_{Predicted\ value}\right)^2$$

It has been demonstrated that models are helpful for the food business in studying the drying kinetics of agricultural items. These models include a variety of statistical measurements (or indicators) that could be utilized to protect the quality of agricultural products and help minimize losses from bumper harvesting and processing. ANN is a relatively recent and straightforward computer modeling approach used for prediction. It is one of the many modeling tools in food technology. It has grown in acceptability and popularity among scientists, researchers, students, and the food business. It is also frequently utilized to solve a wide range of difficult problems in the real world.

VII. CONCLUSION

In summary, we have examined the most popular and up-to-date models for thin-layer drying. We discussed the development of these models and the underlying drying mechanisms. The selection of the most suitable model(s) for the drying processes was accomplished through various statistical techniques, as detailed. However, it is worth noting that the semi-theoretical and empirical models within the category of thin-layer models are the most commonly employed. Utilizing optimization methods, we can predict the optimal models for drying agricultural products in thin layers. These models have proven to be valuable in the food industry for analyzing the drying kinetics of agricultural products, aiding in quality preservation and minimizing losses resulting from bumper harvesting and processing. Additionally, Artificial Neural Networks (ANN), a relatively recent and straightforward computational modeling approach, has gained widespread acceptance among food industry professionals, researchers, scientists, and students. It has become a valuable tool for solving numerous complex real-world challenges.

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