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ANALYSIS TITANIUM DIOXIDE AND ZINC OXIDE IN PHYSICAL SUNSCREEN COMMERCIAL WITH PROTECTION VALUE 35 SPF

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ABSTRACT

This is descriptive research. A descriptive analysis method is a method of explaining symptoms using various variables from the study that are related to one another. This study investigated the shape, size, and composition of TiO_2 and ZnO nanoparticles used in sunscreens to reflect and scatter ultraviolet radiation. The study focuses on the effects of these inorganic substances on ultraviolet and visible light absorption and reflection. XRF, UV-Vis spectroscopy, and XRD were used to analyze TiO_2 and ZnO particles taken from 50-SPF sunscreen. The concentrations of TiO_2 and ZnO in the product were 29.625% and 0.045%, respectively. The sizes of TiO_2 and ZnO are obtained using a systematic equation, with the TiO_2-particle nanosize of 26.31 nm in the form of TiO_2-anorthic respectively. Based on the results obtained, the greater the TiO_2 and ZnO content used, the greater the UV absorbance produced. Maximum absorbance indicates that electrons cannot absorb energy at that wavelength, so the energy is just passed through. Meanwhile, the greater the TiO_2 and ZnO content used, the less reflectance there is in the UV region, and the visible light produced will also increase. Meanwhile, the greater the TiO_2 and ZnO content used, the greater the reflectance in the UV region and the visible light produced.

Keywords : ultraviolet, physical sunscreen, TiO2, ZnO.

I. INTRODUCTION

Long-term exposure to ultraviolet (UV) rays can result in sunburn, skin redness (erythema), skin wrinkles (photoaging), premature aging, and skin cancer [1–4]. A common way to shield the skin from the effects of UV radiation is to apply sunscreen (sunblock) to the skin's surface [5–8]. There are two types of sunscreen: chemical sunscreens that absorb ultraviolet radiation and physical sunscreens that reflect and block UV rays from penetrating the skin surface [9–12]. Due to the active ingredients titanium dioxide (TiO_2) and zinc oxide (ZnO), physical sunscreen may block UV radiation [13–18]. TiO2 and ZnO are two active ingredients found in marketed physical sunscreen products [18–24]. As physical sun protection active ingredients, TiO_2 and ZnO materials offer a wide range of protection because they can reflect and spread UVA (340–400 nm, UVA-II 320–340 nm) and UVB (290–320 nm) rays and effectively block light transmission [16, 24–27]. That is, they function as physical barriers, creating a thin layer that blocks UV radiation from reaching the skin. The ozone layer and atmospheric gases absorb most of the UVC (100–290 nm) light and prevent it from going to the troposphere and reaching the Earth's surface. The ultraviolet energy from the sun that reaches the earth's surface is 95% UVA and 5% UVB [6, 16, 27–29].

UVA radiation increases skin pigmentation because it can penetrate the skin layer deeper into the dermis layer, causing wrinkles (photoaging) to appear [6, 30]. Because UVB light has greater intensity, it is a main cause of sunburn and other serious conditions such as skin cancer [1, 7, 17]. TiO2 and ZnO are white nanoparticles that are non-toxic, odorless, hard to break down under UV radiation, and hard to react with other chemicals. They also don't cause skin irritation, skin sensitivity, material moisture, limited skin penetration, and a wide range of protection [2, 31, 32]. This is because TiO_2 and ZnO are better for sensitive skin than chemicals in sunscreen. This makes it a suitable alternative for people who have sensitive skin or specific skin problems. Rutile, anatase, and brookite are all three main crystal types of titanium dioxide [2, 13, 33–37]. There are also two main types of ZnO crystals, which are wurtzite and zinc-blende. The most common and stable forms in nature are rutile (TiO_2) and wurtzite (ZnO) [14, 38–41]. As compared to rutile, TiO_2 in the form of anatase is the most photoactive. The structure of nanoparticles plays an important role in photocatalytic activity and other properties. In many studies, anatase and rutile have been compared using their ability to form reactive species. Sayes et al. (2006) say that anatase absorbs water molecules that are no longer connected, while rutile absorbs water molecules that are still connected. This means that anatase is more than capable of reacting with reactive OH species under UV light [42].

ZnO's bleaching effect is lower than that of TiO_2. ZnO is an n-type, wide-band semiconductor. The band gap energy of wurtzite is 3.22 eV, so it's 0.1 eV lower than that of the zinc blend (3.32 eV). TiO_2 and ZnO in sunscreens might cause white patches on the skin. These substances have large particle sizes, mostly above 200 nm, which allow reflection not only in the UV spectrum but also up to visible light. Therefore, sunscreen manufacturers use both of these materials in nanoparticle size to enhance their UV filters for commercial sunscreen products and radiation absorption for other skin care products [17, 32, 35, 43–45]. Mie's law is used to determine the nano-size of particles that provide the best protection at a particular wavelength using the following calculations: The best radiation effect decreases at a wavelength of 290 nm (UVB) in particles 20–100 nm, 350 nm (UVA) in particles 80–160 nm, and 400 nm (UVA) in particles 120–180 nm [46]. Particles with sizes between 15 and 50 nm can reflect light in the UV-Vis spectrum, creating something of a reduced color [47]. Solar radiation is greatly impacted by the dimensions and breadth of nanoparticle surfaces [48]. Mie's law provides a generic solution to radiative diffusion, while Rayleigh's interference connects the intensity of particle-file distortion for quite small particles with intensity at a particular wavelength. According to Rayleigh's distortion, the intensity of the scattered radiation is inversely related to the four-tier wave length. Therefore, the smoother the particle, the better it disperses UV at wavelengths below 400 nm [49]. Another study said that TiO_2 and ZnO were safe to use because they could not penetrate the skin at a certain size [43]. The National Agency of Drug and Food Control (NADFC) regulation No. 17/2022 and the US FDA say that the maximum amount of TiO_2 and ZnO that may exist in sunscreen is 25% [31, 44, 50–55].

The bigger the percentage of TiO_2 used, the greater the resulting absorption intensity. This is important because the greater the total absorbance intensity, the more effective it will be, so long as it maintains the FDA and BPOM limits, including 25% for TiO2 and ZnO. According to Kusumawati's research from 2017, the amount of TiO_2 in a product effects how much UV radiation it can absorb [56]. This is because anti-UV materials will have a better absorption capacity when present in greater quantities. However, there is no comprehensive information available regarding the percentage composition of the inorganic chemicals present in commercial sunscreen products that use TiO_2 and ZnO. The inability to focus on the amount of TiO_2–ZnO present in commercially available physical sunscreens, which has an impact on absorption and reflectance in the ultraviolet and visible light regions, is a flaw in earlier studies. In this research, we analyzed inorganic substances found in sunscreens marketed commercially and commonly used in tropical climates. Some steps will be taken, such as figuring out how the inorganic compounds in these products are put together. Since the concentration of the active ingredient hasn't been found yet, a test of the concentrations or contents of each of these active substances is needed. Second, perform absorption and reflection tests to determine an appropriate sunscreen. Finally, the distribution of the size and phase of the TiO_2 and ZnO crystals on the products was evaluated. We have the information required to develop our own products using this data.

II. METHOD

This is descriptive research. A descriptive analysis method is a method of explaining symptoms using various variables from the study that are related to one another. The samples analyzed are commercially available physical sunscreens with unknown constituents that are commonly used by nations in tropical climates or have a protection value of 50 PA++++. The product is a primary sunscreen, which means the primary goal is to protect consumers from UV radiation [57, 58]. A sample of 1 gram of cream is put into the sample box and arranged on a spoon to keep it even. The X-ray Fluorescence (XRF) is then measured without treating the sample. The result of the data analysis is that the composition of the elements obtained is only 100 percent oxide. It is intended to calculate the amounts of TiO_2 and ZnO nanoparticles based just on the data gathered from the XRF instrument.

Second, the Visible Ultraviolet Spectrophotometer (UV–Vis) is used to determine the absorption and reflection values of each solar panel. The amount of TiO_2 and ZnO nanoparticles in the sun protection has an influence on the absorption and reflection values. There are nonetheless other compounds that have increased absorption and reflection values, but in this study, we concentrated on estimating the values from the percentage of TiO_2 and ZnO nanoparticles in sunscreen. Around 1 gram of cream is put in the sample receptacle, and a spatula may be used to equalize. The UV-Vis spectrum is then measured without the substance being modified. UV-Vis spectrum measurement is carried out at wavelengths ranging from 185 nm to 700 nm in the ultraviolet and visible light spectrums. Third, X-ray diffraction (XRD) is used to test the size and shape of TiO_2 and ZnO crystals. In general, the active ingredient TiO_2 used in the manufacturing of sunscreen is rutile. Rutile TiO_2 has beneficial UV reflection and poor absorption abilities. The rutile effect of TiO_2 protects against UV rays more than the anatase effect of TiO_2. Therefore, nano TiO_2 is employed in skincare more often compared to anatase.

X-ray fluorescence is one of the characterization instruments that uses X-ray interaction to determine the composition of an element in a material. In addition, X-ray fluorescence is included in the non-destructive analytical techniques used to identify and determine the concentration of elements in solid, powdered, or liquid samples. The analysis using X-ray fluorescence is carried out based on the identification and detection of the characteristics of x-rays that occur from photovoltaic effect events. Photoelectric effects occur because electrons in the sample atoms are exposed to high-energy fields. The result of X-ray fluorescence data is a spectrum of the comparison of excitation energy to the intensity of x-rays. Excitation energy shows the sample component and the intensity of the quality value of the element. The higher the intensity, the higher the percentage of the element in the sample. The X-ray fluorescence method gives a value for the total intensity of a particular element in all forms of compounds. The UV-Vis spectrophotometer is a device used to measure transmission, reflection, and absorption as a function of wavelengths, as well as for measurements in ultraviolet and visible areas. The UV-Vis spectrophotometer is an analysis method that uses wavelengths and visibility as an absorption area to detect compounds. The spectrum emitted by the UV-Vis spectrofotometer is wide and usually shows only a few peaks. The peak is the wavelength at which the maximum occurs. Figure 1 shows the flowchart of this study.

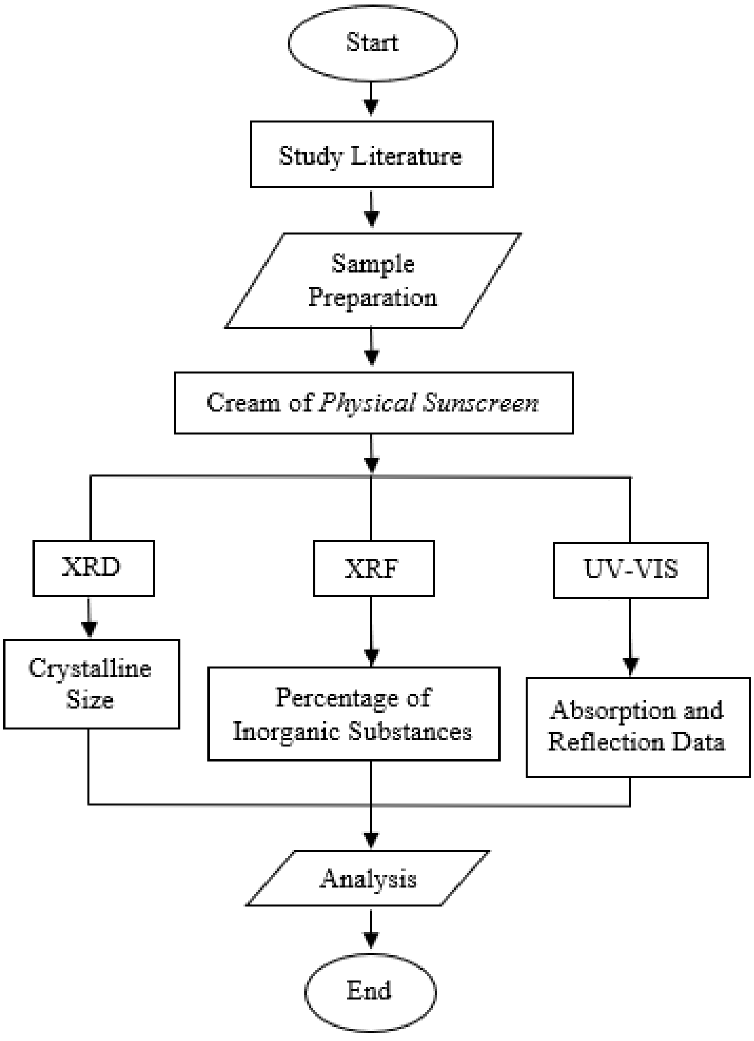

Fig 1. Flowchart of this study

The following equation can be used to determine the percent of radiation using the sun's radiation emission percentage:

$$A + R + T = 1 \quad (1)$$

A = Absorbance
R = Reflectance
T = Transmittance

Using the XRD PANalitycal XPERT Pro with Cu Kλ radiation for testing The test sample is inserted into the sample container that is provided so as to analyze the phase composition. Crystals are used in some of the following formulas:

$$D = \frac{K\,\lambda}{\beta\ cos\theta} \quad (2)$$

where D is the crystal's size, is the wavelength of the x-rays, and is the Bragg angle. The parameter β can be defined as follows:

$$\beta = (B^2 - b^2)^{1/2} \quad (3)$$

where B indicates one of the linewidths of the most intense TiO_2 diffraction [57].

III. RESULTS AND DISCUSSION

In testing the content of the compositions of TiO_2 and ZnO in the sample using X-ray Fluorescence PANalytical Epsilon3 instrument, we obtained the data in Table 1.

Table 1. Oxide Substances in Commercial Physical Sunscreens

Material	Percentase (%)	Maximum FDA approved concentration (%)	Peak absorption Wavelength (nm)	Range of Protection (nm)	Protection provided (UVB/UVA)
TiO_2	29.625	25	Varies	290–350	UVB UVA II
ZnO	0.045	25	Varies	290–400	UVB UVA I
Al_2O_3	3.212	-	-	-	-
SiO_2	34.704	-	-	-	-
CaO	5.115	-	-	-	-

P_2O_5	20.858	-	-	-	-
V_2O_5	0.243	-	-	-	-
Fe_2O_3	0.091	-	-	-	-
K2O	3.192	-	-	-	-
Ag_2O	1.504	-	-	-	-
Cl	1.409	-	-	-	-

After that, X-ray diffraction was utilized to determine each crystal phase and the size of TiO_2 and ZnO nanoparticles used in solar products. XRD test results are shown in Figure 2.

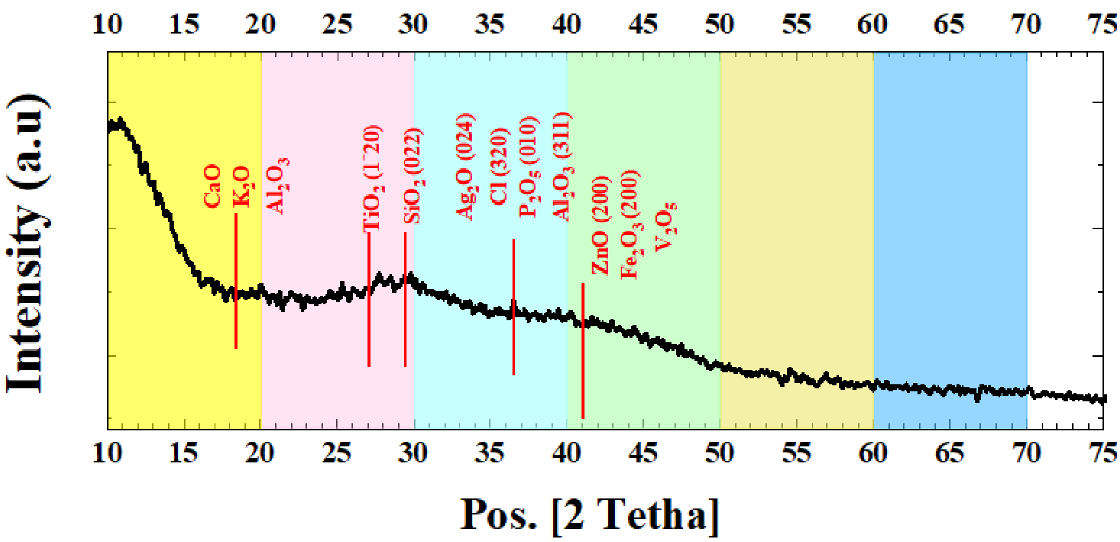

Fig 2. Sample diffraction using XRD

Based on the XRD data, the peak of TiO_2 is at position (2 tetha) of 26.35^o with the miller index $(1^{-}20)$. Through systematic computation, the crystal size of 26.31 nm and the anorthic crystal were reached with the FWHM number 0,3070. The difraction peak for ZnO position was not found, so miller index, size, ZnO crystal shape, and FWHM number could not be identified. TiO_2 and ZnO in sunscreen work by reflecting or dispersing UV radiation and visible light in a broad wavelength spectrum [60]. ZnO provides better UVA protection, as TiO_2 gives better UVB shielding and has a whiter effect because of its greater refractive index [61]. 10–50 nm TiO_2 and ZnO nanoparticles can reduce visible light refraction and increase cosmetic product approval above 200–500 nm as non-micron dim. They can also absorb UV radiation, but the range of UV particle absorption shifts to shorter wavelengths than UVA. Furthermore, tiny microparticles have the ability to coagulate, decreasing the effectiveness of sunscreen creams. To prevent it, they are coated with aluminum or silica, which prevents the formation of free radicals and enhances photostability. In the sample absorption testing using the Ultraviolet–Visible Spectrophotometer type Specord 210 Plus Analytic Jena, the resulting graphical information was obtained or given in Figure 3.

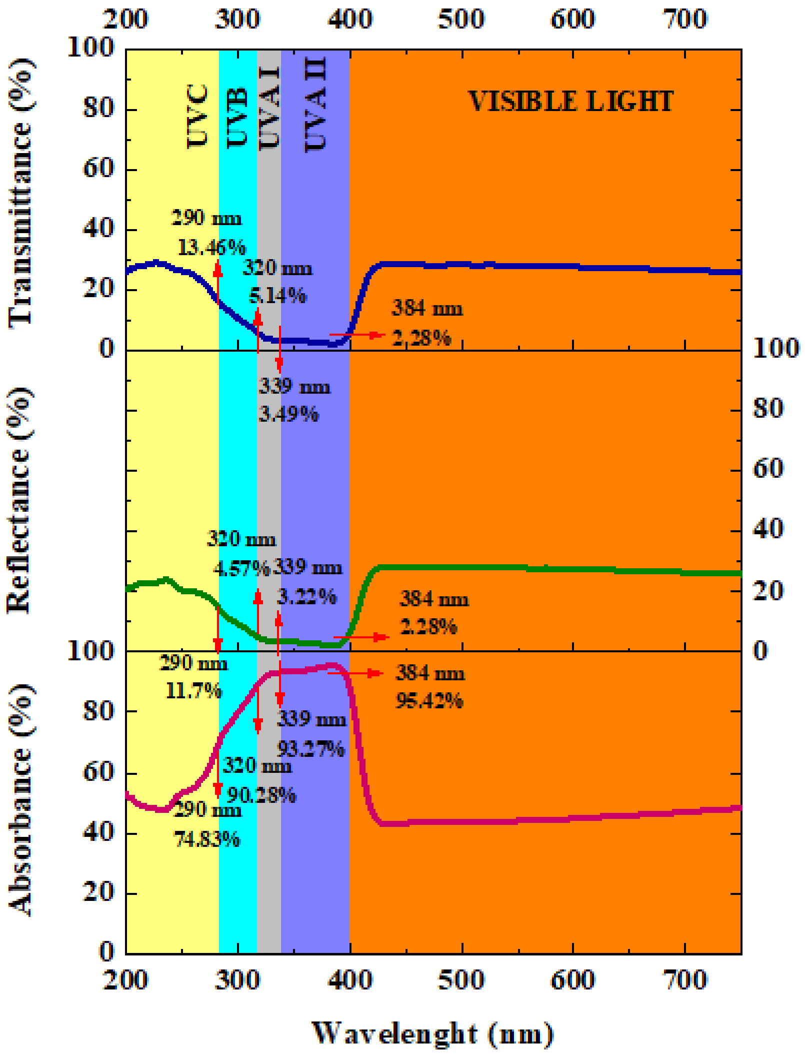

Fig 3. Absorption (%), Reflectance (%), and Transmittance (%) sample using UV-VIS Spectrophotometer.

UVC radiation is greatest at a wavelength of 290 nm, where sunlight absorbs 74.83%, reflects 11.7%, and allows within up to 13.46% transmits of UVC rays. The peak of UVB radiation is at 320 nm wavelength, while sun protection absorbs 90.28%, reflects 4.57%, and transmits as much as 5.14% of UVB rays. The peaks of UVA I and UVA II radiation are successively located at wavelengths of 339 nm and 384 nm, where the sunscreen absorbs 93.27% and 95.42%, reflects 3.22% and 2.28%, and transmits 3.49% and 2.28% of UVA I and II radiations. A good physical sunscreen has low absorption and great reflectance in the UV region. In order to provide the best possible protection to its users. If this high reflectivity reaches the visible light area, the human eye will see scattered light through the sunscreen used. This phenomenon is known as the whitecast effect. Whitecast is caused by the use of tiny TiO_2 or ZnO particles.

According to the findings in Table 1, concentrations of TiO_2 and ZnO may still be tolerated below the highest allowed level. In XRF testing, several oxides were found contained in the physical sunscreen being tested. From the XRF test results, data was obtained on the percentage of inorganic substances used in physical sunscreen. The resulting elemental composition data obtained is only calculated as one hundred percent oxide. The test was not given any treatment; it was intended to calculate the levels of TiO2 and ZnO nanoparticles purely through XRF readings. According to the U.S. FDA, TiO_2 can provide protection against UVB and UVA II, and ZnO can provide protection against UVB and UVA I. Meanwhile, the maximum allowable limit for TiO_2 and ZnO is 25%, but based on the data obtained, the composition of TiO_2 used by the sample exceeds the permitted threshold. Meanwhile, the composition of ZnO in several products used is very small. One of them is crystalline TiO_2 or ZnO. By using equation 2, we can calculate the crystal size of the XRD data. The crystalline size of TiO_2 in the sample is 26.31 nm. Meanwhile, the ZnO content in the sample was not detected. According to theory, if the diffraction peak is sharp, it means the crystalline size is large, whereas if the diffraction peak is short and wide, it means the crystalline size is small. According to experts, TiO_2 can trigger free radicals and accelerate the premature ageing process. So sunscreens that use inorganic substances have a high risk of causing damage to the skin. Other substances found in products are Al_2O_3 and SiO_2. In sunscreen products, these substances function as coatings for these inorganic substances to reduce the formation of free radicals and increase photostability. This makes it possible to make inorganic substances that exceed this maximum threshold, making them safe when used.

According to theory, the greater the TiO_2 and ZnO content used, the greater the UV absorbance produced. Meanwhile, the greater the TiO_2 and ZnO content used, the lower the reflectance in the resulting UV area. TiO2 nanoparticles absorb more UVB radiation, while ZnO absorbs more UVA I radiation, even though ZnO's energy strip gap exceeds that of TiO2. One of the known negative properties of TiO2 and ZnO in sunscreen products is the appearance of white spots on the skin, which are called white cases because their size is mostly above 200 nm, thus allowing reflection not only in UV ranges but also up to visible light. Based on experimental results, the size of the nanoparticles does not exceed 100 nm, so the white case is not very visible to the eye when using sunscreen. Based on the results obtained, the greater the TiO2 and ZnO content used, the greater the UV absorbance produced. Maximum absorbance indicates that electrons cannot absorb energy at that wavelength, so the energy is just passed through. Meanwhile, the greater the TiO2 and ZnO content used, the less reflectance there is in the UV region, and the visible light produced will also increase. This result is as concluded by research conducted by Kusumawati (2017).

IV. CONCLUSION

The research concluded that the higher the TiO_2 and ZnO concentrations, the higher the UVA absorption. Meanwhile, as the TiO_2 and ZnO concentrations increase, ultraviolet reflectance and visible light production decrease. However, this trend cannot be used as a reference because commercial physical sunscreen includes complex components, namely different oxide components such as Al_2O_3, SiO_2, Pb_2O_5, CaO, Cl, Fe_2O_3, K_2O, and V_2O_5. And this oxide, like TiO_2 and ZnO, functions as a semiconductor, causing the creation of free radicals through photocatalytic processes, as well as other sunscreen supporting materials, which may impact absorbance, reflectance, and degradation. The ideal product for standardization is one that is under the FDA and BPOM percentages, offers low absorbance and high reflectance, and offers minimal degradation rates. Based on this statement, this sample does not match the specified requirements.

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