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Application of Keratin Biopolymer in the Textile Industry

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Abstract: Keratin is one of the most abundant biopolymers derived from animal sources, with a significant contribution from by-products of the cattle, ovine, and poultry industries, providing numerous potential to manufacture cost-effective and sustainable advanced materials. Even though many reviews have examined keratin use in polymer-based biomaterials, little attention has been paid to its potential in conjunction with other polymer matrices. As a result, we give an exhaustive literature analysis describing keratin's compatibility with other synthetic, biosynthetic, and natural polymers, as well as its effect on the final properties of the materials in various applications, especially in the textile industry.

Keywords: keratin; biopolymer; extraction; wool; feathers; textile applications.

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1. Introduction

The term "polymer" is derived from the Greek words πολυ (polu) for "many" and μ_ερος (meros) for "part," referring to a continuous chain made up of many components. The combination of repeating units to form long chains of widely varying length and structure is critical in determining the properties and applications of the resulting polymers, as the diversity of polymer properties is attributed to the fact that each polymer molecule consists of many parts with individual variations in repeating unit sequence and chain length [1].

Biopolymers are classified into three types based on their origin: (a) polymers derived from a renewable resource/biomass, such as agro-polymers derived from agricultural resources; (b) polymers derived from microbial products or animal origin that may be useful in medical and pharmaceutical practices, and (c) chemically synthesized biodegradable polymers derived from petrochemical resources or modified from natural polymers. The characteristics of biopolymers are determined by the basic materials, additives, and modifications made during production. The capacity of biopolymers to be extinguished without emitting harmful residues is the most significant benefit associated with the usage of biopolymers, given the growing importance of environmental preservation [2].

2. Keratin as a Biopolymer

Keratin is a component of the fibrous protein family. Keratin is primarily found in waste from the wool industry, slaughterhouses, and meat markets [3]. Chicken feathers are regarded as one of the most important sources of keratin. The disposal of feathers in landfills generates

numerous environmental problems [4]. Hoof keratin has shown encouraging outcomes in tissue engineering and biomedical applications [5]. Keratin is used in a variety of industries, including cosmetics, pharmaceuticals, biomedical, fertilizers, feedstock, environmental remediation, leather and textile processing, bioplastic films, coating, films, packaging, biodegradable composites, drug delivery, surgery and repairing, filter membrane and resins, bio-cement, and bio-ink [6-9].

Keratins are insoluble fibrillar proteins generated in vertebrate epithelial cells and fulfill structural, protective, and cell differentiation roles [10,11]. These proteins are classified into three classes based on X-ray analysis data developed in the last century: alpha-, beta-, and gamma-keratins [12,13].

Alpha-keratins are abundant in the epidermis of all vertebrates, mammalian epidermal derivatives, and some avian and reptile appendages. These proteins' secondary structures are densely packed with alpha-helices. The polypeptide chain produces a hydrogen bond with the maximal possibility of contact between one amino acid's carbonyl group and another amino acid's amino group in the alpha-helices configuration. The alpha-helix structure has a diameter of 7-10 nm and a molecular mass of 40-68 kDa [14,15]. Alpha-keratin is found in abundance in animals. Such a structure is arranged as a coiled coil and participates in a compact structural arrangement to elongate the polypeptide chain. Beta-keratin molecules form beta layers wrapped in helices and are found in the integument of birds and reptiles. Conversely, the beta-structure has intermolecular hydrogen bonding between the carbonyl and amino groups. The diameter of the beta-structure is approximately 3-4 nm, and the molecular mass is approximately 10-22 kDa. These structures are most common in reptile tissues, such as feathers, claws, and bird beaks [16]. Gamma-keratins are amorphous matrix proteins that contain alpha-keratin filaments. However, recent evidence has prompted us to reevaluate this state of affairs. Only alpha keratins are members of the intermediate filament (IF) protein superfamily [17].

The potential of alpha-keratins to transition from alpha- to beta-conformation under specific physical factors (heating, mechanical stress) has been demonstrated, allowing them to be referred to as "beta-keratins" [18]. As a result, only alpha- or IF-keratins are currently considered real keratins, while beta-keratins are referred to as corneous beta-proteins (CBPs) or keratin-associated beta-proteins [19-21]. According to the most recent research, proteins previously known as gamma keratin (now more often keratin-associated proteins (KAPs)) are not homogeneous glassy material but have a well-defined granular structure [22]. CBPs and some KAPs (for example, filaggrin and trichohyalin) are encoded by genes from the epidermal differentiation complex, confirming the lack of a phylogenetic link with IF-keratins [21,23]. Alpha and beta keratin are illustrated in Figure 1, and a comparison between them is in Table 1. [24, 25].

Table 1. Comparison of alpha and beta-keratin based-structure.

Characterization	Alpha-Keratin	Beta-Keratin
Bonding	Intramolecular hydrogen bonding	Intermolecular hydrogen bonding
Diameter (nm)	7-10	3-4
Structural features	Intermediate filament matrix	Amophorous matrix
Molecular mass (kDa)	40-68	10-22
Distribution	Wool, horns, hairs, nails and hooves	Avian beaks, feathers, claws, reptilian epidermis
Stiffness	High	Lower than alpha-keratin

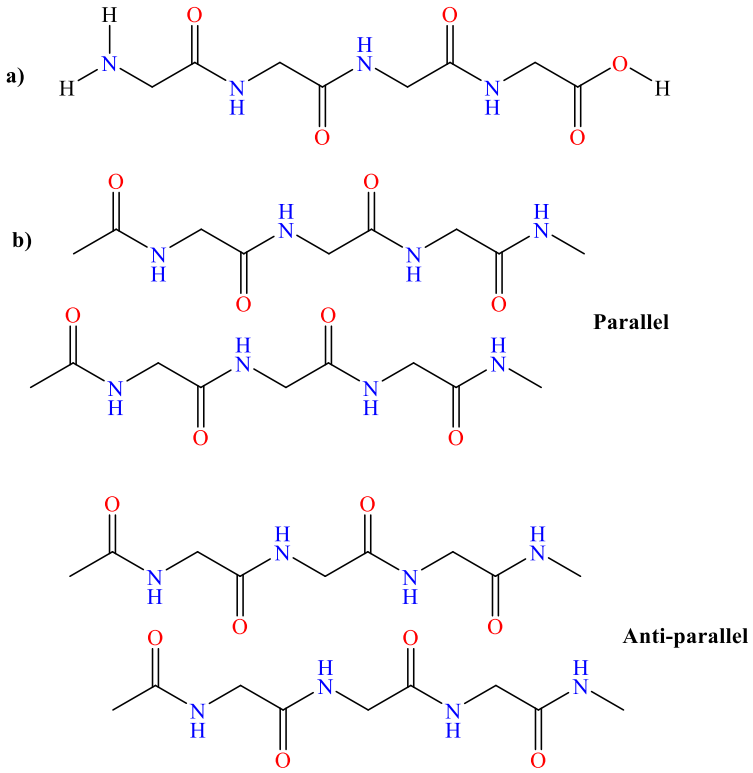

Figure 1. a) α-keratin (α-helix) and b)β-keratin (β-pleated sheet)

3. Sources of Keratin polymer

Keratin has been obtained from chicken feathers, beaks, claws, nails, horns, hooves, human hair, and toenails over the years. Wool is another important source of keratin. Wool containing up to 95% keratin by weight is regarded as a pure source of intermediate filament proteins, which have grown in relevance in the aesthetic and biological industries. Keratin biomaterials derived from wool and human hair have cell-binding motifs with hemostatic and cell-binding properties. Keratin can self-assemble and create polymers by itself. These biomaterials are biocompatible and capable of cellular proliferation, making them ideal for drug delivery systems and tissue engineering. They have also discovered potential positions in the energy and agricultural sectors, as well as the pharmaceutical and cosmetic industries, as well as the leather and textile industries. [24].

3.1. Wool keratins.

Wool is a great animal fiber because it contains 82% keratinous protein. Wool keratins are separated into two fractions: low sulfur, represented by intermediate filaments, and high sulfur, represented by KAPs. There are two types of IF-keratins: type I (acidic keratins) and type II (basic keratins). These proteins have molecular weights ranging from 40 to 70 kDa. The C- and N-terminal domains, as well as the alpha-helical rod domain, are all present in their structure. Molecules of type I and type II keratins form heterodimers with a left-handed coiled-coil structure that is maintained in the rod domain by the presence of heptad repeats rich in apolar amino acids such as leucine, isoleucine, and valine. The complete intermediate filament is made up of four protofibrils, which consist of two protofilaments and two keratin heterodimers. [7,17,26,27]

Wool keratins' C- and N-terminal domains are involved in creating disulfide linkages with matrix proteins. The amino acids included in KAPs found in the matrix include cysteine,

proline, tyrosine, and glycine [28]. Wool keratin is a robust substance suited for biological applications because of disulfide bonding and other structural properties. It is frequently utilized in textile applications and is scientifically significant due to its mechanical and structural properties.

3.2. Feathers' keratins.

Humans have been fascinated with the concept of how birds can fly and how birds (like ducks) can protect their wings when swimming or in rainy conditions since very early times. You may have seen that the bird's wing does not easily become sloppy during the rain or wet season [29-31]. As a result, keratin (beta-form) protein may be involved in providing mechanical support to the feather, preventing it from becoming sloppy. Examine feathers under transmission electron micrographs to better comprehend this notion, and their findings disclose the filament-matrix structure with -keratin filaments. This structure had a diameter of around 3 nm and was embedded in an amorphous matrix. The keratinous material is also present in the rhamphotheca (outer surface layer) of bird beaks, allowing the beaks to perform a range of roles, including feeding, social interactions, fighting, and grooming [32]. Except for the toucan beak, which is both thick and long, bird beaks typically fall into two categories: (1) long thin and (2) short/thick [14,27,33].

3.3. Stratum corneum, horns, and hooves.

The interplay of light and skin affects the optical visibility of the skin to the human eye. Skin can absorb and reflect light in various ways [34]. Skin also regulates the body's temperature and plays an active role in the defensive process by functioning as a barrier for pathogens (s). The outermost layer of the stratum corneum covers mammalian skin, and its thickness ranges between 20 and 40m [35]. This layer serves as a defense layer against external attack (predators) and as a diffusion barrier [36].

Keratinocytes make up the stratum corneum, and these cells are embedded in a lipid-rich intracellular matrix. Their cytoplasmic content is organized in a web-like structure and integrates strongly at cell-to-cell contacts. Such interaction(s), when diversely combined, maximize mechanical support [37].

Cattle, waterbuck, sheep, buffalo, and gazelle all carry keratinous material as a horn. Horns are used as a weapon, as a shield against predators, and in a fight with other animals for defense. Hooves are the toughest keratinous materials and remain an appealing study topic. The hoof wall is made up of flattened keratinocytes. Hooves have a complicated structure, which enables the hoof wall to absorb enough energy as the crack deepens [38].

3.4. Nails and hair.

Nails are a significant source of -keratin. It covers the extremities of the fingers and toes in primates and a few mammals (their ends have soft skin; thus, these proteins help in protection indirectly). This protein generates curled claws in cats and exhibits a -type pattern during X-ray diffraction study [39]. Fingernails are an important feature in primates because they can be used for fighting, clawing, and opening objects [40].

4. Extraction of Keratin Polymer

Several hydrolytic and non-hydrolytic techniques have been used to extract keratin from natural resources [41]. Most such techniques use oxidizing or reducing agents in the presence of auxiliaries like sodium dodecyl sulfate, urea, and EDTA [42-45]. Another study discussed the extraction of keratin, and poultry feathers were dissolved in a deep eutectic solvent (choline chloride (ChCl) and oxalic acid (OA) combined in a specific molar ratio) and deionized water. The water-soluble and insoluble extraction fractions were obtained and separated after dissolving, dialysis, and filtering [46,47].

The alkaline hydrolysis process can be used to produce keratin from bird feathers. Chemicals such as ammonium sulfide or sodium sulfide can decrease the disulfide group to the thiol group throughout the procedure. Furthermore, the free-SH group can be partially changed by employing -mercaptoethanol. The treatment lasted 90 minutes at 45-80°C. The obtained keratin molecular weight ranged between 1 and 11 kDa [48,49], demonstrating the effect of thermochemical treatments with different reducing agents (2-mercaptoethanol, dithiothreitol, sodium m-bisulfite, sodium bisulfite, and sodium hydroxide) on keratin synthesis (in chicken feathers extract). Treatment with 2-Mercaptoethanol and sodium bisulfite produced approximately 84% and 82% keratin, respectively. Furthermore, sodium hydroxide (2.5%) increased keratin synthesis by up to 94% [49,50].

Solid-state fermentation (SSF) is a growing industrial process in the biotechnology and microbiology fields; it is mostly utilized for large-scale recycling or renewal of biological waste(s). Microorganisms develop in this technique in an aqueous-free environment or sometimes with very little water content [51]. Submerged fermentation is a solid-state fermentation analog in which all natural circumstances are optimized, and the environment is mimicked [52,53]. Chitturi and Lakshmi [54] present an appealing approach for producing keratinase utilizing Bacillus strains. This study's favorable attribute was a better method for keratinase production, and the yield was enhanced from 283-367 KU/mL to 415-442 KU/mL. Under appropriate conditions, the keratinase enzyme can be produced from bacterial cultures and fungal cultures, as it significantly impacts feather breakdown. SSF is an environmentally benign process that greatly reduces bio-pollutants and expands the space available for food industries [52,55].

5. Properties of Keratin Biopolymer

Horns, wools, nails, feathers, and hooves are a global class of biological co-products representing cysteine-rich filament-forming proteins. Furthermore, keratins are the proteins that form a shielding layer for epidermal appendages, playing a vital role in defense. The disulfide overpass's expansive arrangement substantially impacts keratin qualities, particularly broad chemical and mechanical resistance. Keratin is insoluble in both hot and cold water, which helps to inhibit digestion by proteolytic enzymes such as pepsin, papain, and trypsin [25,56-58]. The richest compartment for keratinous structural protein is the cytoplasm of epithelial cells, where they were organized into a network of 10-12 nm broad intermediate filaments [59]. Nearly 54 conserved genes in the human genome encode keratin protein, which is further classified into type A and type B subgroups of intermediate filament (IF)-encoding genes. There are 28 types of A genes and 26 types of B genes, with each type encoding a single polypeptide chain. Type A proteins are smaller and more acidic, whereas type B proteins are larger and more alkaline [60]. Type A and B proteins combine and create a heterodimer,

stimulating keratin polymerization. Keratin arrangement is governed by type A and type B genes and thereby maintains the integrity of epithelial cell lines; nevertheless, inappropriate keratin arrangement and misfolding can lead to severe epithelial illness such as epidermolysis bullosa simplex [61,62].

6. Applications of Keratin Polymer in the Textile Industry

6.1. Keratin in printing textiles.

A recent eco-friendly binder for pigment printing on textile fabrics was made using keratin. The keratin-based binder is bio-binder and cost-effective. It was successfully used in blends of polyester/acrylic and polyester/viscose, as well as polyester/polyacrylonitrile, viscose, and pigment [63]. This binder is a safe substitute for the industrial synthetic binders that are typically used in textile pigment printing. The printing pastes with keratin-based binders were exposed to rheological studies, demonstrating that they are non-Newtonian pseudoplastic. By applying a crosslinker like glutardialdehyde, the pigment-printed samples with keratin-based binders achieved the highest K/S values and fastness characteristics. The K/S values of the printed fabrics employing keratin-based binders are comparable to those obtained using a commercial binder for identical printing operations. All printed textiles have excellent light, wash, and perspiration fastness properties [64].

6.2. Keratin in textile dyeing.

Keratin was extracted from cheap, coarse Egyptian wool fibers using a simple process. Because extracted keratin is a natural proteinic biopolymer, it may be colored with both reactive and acid dyes by crosslinking it with wool. To do this, the wool was treated with a keratin/ECH mixture, which reduced the amount of color in the effluent. The dyeability of treated and untreated wool materials has been examined in relation to various dyeing conditions. Epichlorohydrin can be utilized to crosslink the biopolymer keratin to wool indefinitely. The dyeability of treated wool has been increased by utilizing mono-sulphoni and disulphonic acid reactive dyes, as well as vinyl sulphone and bromoacrylamide reactive dyes. Keratin is a biodegradable protein that can be utilized as an alternative to other unwanted chemicals used in wool chemical processing. More research is being done to see if keratin can be applied to particular synthetic fibers to achieve specific coloring qualities.

Keratin macromolecules, being proteinic, should chemically attach to wool. Epichlorohydrin is used as a crosslinker to ensure that keratin is permanently crosslinked to wool. The effect of keratin/ECH treatment on the dyeability of wool using the acid dye Supranol Blue BLW (C.I. Acid Blue 203) at various temperatures (40°-85 °C) has been studied[65].

The dye bath used in dying prepared wool test materials with Acid Blue 203 is practically exhausted within 5-30 minutes, depending on the dyeing temperature. This period is substantially shorter than required to completely exhaust the dyebath when dyeing untreated wool fabric with the same dye. The dye bath is completely exhausted after half an hour of preparation of wool fabric before dying at room temperature or after 5 minutes of dyeing at 60°C [66].

Such observations can be described in terms of keratin's ability to make persistent crosslinks with wool polypeptide chains. The increased amount of cationic groups in the treated

wool resulted in increased anionic acid color absorbability. Keratin, as a protein with several amino and amide groups, has enough cationized basic nitrogen-containing groups in an acid medium to bond with the anionic sulphonic groups in the acid dye, as demonstrated below: $HOOC–W–NH_2$ +Cl–ECH–OH +$HOOC–K–NH_2$ =(Wool) (Crosslinker) (Keratin) HOOC–W–NH–ECH–OOC–K NH_2 [66]

6.3. Keratin in textile finishing.

Patankar *et al*. make a study about a novel technique for utilizing chemically processed keratin generated from wool waste as an effective flame retardant for cotton fibers that contain nitrogen and phosphorus. The sources of nitrogen and phosphorus applied were sodium pyrophosphate and melamine, while the crosslinking agent used was glyoxal, as illustrated in Figure 2. TGA confirmed the enhanced thermal stability of the modified wool waste keratin and treated cotton fabrics, while FTIR and XRD investigations demonstrated the structural changes. The modified wool waste keratin produced a continuous, unbroken layer of char that gives treated cotton flame retardancy due to the synergistic effects of nitrogen and phosphorous. Compared to untreated cotton, the modified keratin application to cotton's limiting oxygen index increased flame retardancy by about 66.7%. Overall, the research results demonstrate a sustainable method for the textile industry that combines waste management components to enhance the value of one textile sector while lowering solid waste from the wool business (multifunctional textile finishing agent for the cotton industry) [67, 68].

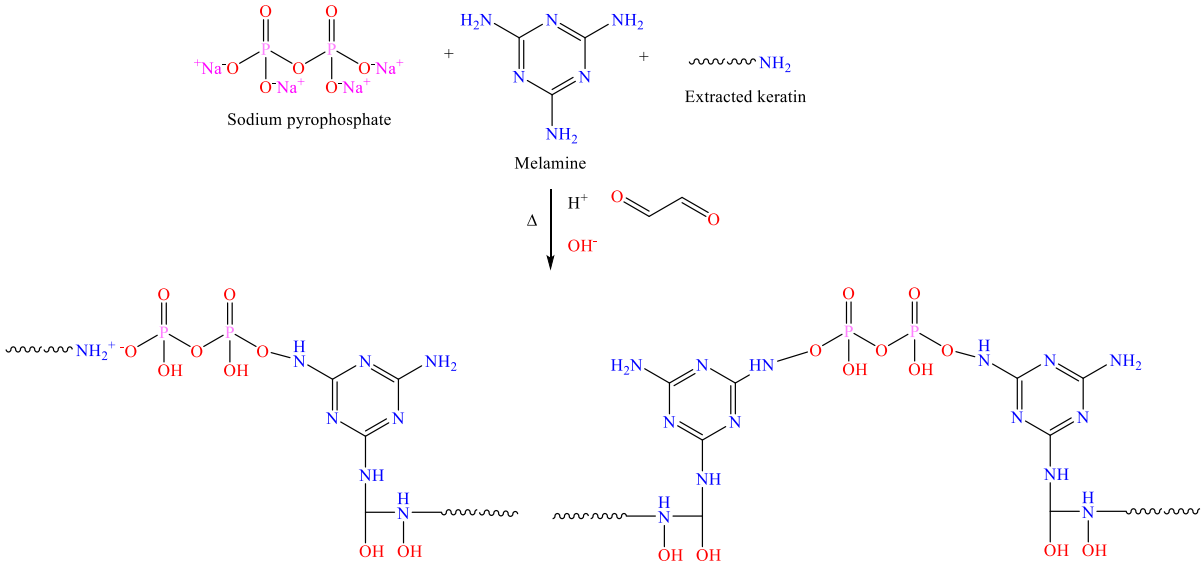

Figure 2. Reaction mechanism of extracted keratin with Melamine and Sodium pyrophosphate

The immobilization of amino acid residues on partly carboxymethylated cotton nonwoven textiles in this study provides a novel wound treatment (CM-CN). To overcome the lack of ability to protect an open wound from infection, a standard cotton nonwoven fabric was chemically changed using a pad-dry-cure approach that included a carboxymethylation procedure. Following that, chicken feather wastes were used as a natural source for the cationization of CM-CN using the same process. Keratin was extracted satisfactorily from chicken feathers using both chemical and enzymatic techniques. The tensile strength increased by 200%, the air permeability nearly doubled, and the changed samples showed the quickest cell growth. According to the conclusions, enzymatic extraction had an impact, and the samples coated with enzyme-extracted keratin demonstrated improved characteristics suited for wound dressing applications [69, 70].

6.4. Keratin in technical textile applications.

Chicken feathers are biopolymers of fiber and quill that comprise 91% keratin, 1.3% fat, and 7.9% water. Feathers have several desirable features in the textile industry, including high compressibility, very low density, high durability, and warmth retention. Because of these characteristics, feather fibers are an excellent supply for technical textile manufacture. Feather fibers are lighter and smaller in diameter and length than wool fibers, resulting in a substantially larger surface area. The larger surface area is desirable, but the shorter length makes feathers unsuitable for spinning on standard woven textile gear. As a result, nonwoven textiles are frequently made from chicken feathers.

Although the short length of feather fibers rendered spinning yarn and weaving fabric with typical machinery nearly difficult, various attempts have lately been made to manufacture feather-based textiles [71]. Manufacturing nonwoven fabrics from feathers is a more difficult procedure than wool processing. The feathers are gathered and rinsed with a polar organic solvent before being dried and shredded to remove the quills, frequently using a turbulent airflow. Nonwovens are then created by combining the spray-bonding process with chemical bonding [72]. There are a few examples of textile fabrics made from feather fiber. Because of their smaller diameter and relatively high surface area, feather fibers are viable for filtration applications, such as air filtration, vacuum cleaning, or drinking water. Feather fibers have also been found in studies to be effective at separating several heavy metals from water, including copper, lead, chromium, and mercury. Feather-based fabrics have also been used in the automobile industry for seat cushions and home decorating [73].

Geotextiles are utilized for separation, drainage, filtration, anti-erosion sealing, and improving plant vegetative conditions. This study aimed to see if adding poultry feathers accelerated nonwovens' biodegradation in cultivated soil. The tests were conducted in a laboratory setting and were based on a weight loss assessment. The investigations verified the beneficial effects of keratin-rich waste on the time required for the biodegradation of the studied materials (the biodegradation period was 8–24 weeks). Furthermore, the effect of biodegradation of the studied materials on ecotoxicity was investigated and shown to have no detrimental effects on microbiological activity (106 CFU). The carbon-to-nitrogen ratio of the test medium was also determined as part of the investigation (blank, 12–14:1; with feather addition, 19–20:1). A statistical investigation established a link between mechanical parameters and biological degradation time. This study was essential to better manage poultry feather waste in agricultural applications. The studied materials appear to be a gold solution that not only permits the delivery of critical nutrients to the soil but also controls trash in an environmentally safe manner [74].

7. Summary

Keratins are common, ranging from large components of home dust to prevalent contamination in laboratory protein analyses. Keratin is the principal structural fibrous protein that forms many different animals' hair, wool, feathers, nails, and horns. It contains a high quantity of cysteine, 7-20% of the total amino acid residues, which forms inter- and intramolecular disulfide connections. Keratin wastes are considered environmental contaminants and are mostly produced by chicken farms, slaughterhouses, and the leather industry.

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Conflicts of Interest

The authors declare no conflict of interest.

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