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THE ROLE OF PH BALANCE IN HAIR COLORING AND LIGHTENING: A REVIEW OF MODERN DYE FORMULAS

Summary. *This article examines pH-dependent mechanisms of hair coloring and lightening at the cuticle and cortical matrix levels, with a focus on comparing alkaline permanent systems, demi-permanent solutions, and acidic formulas. This research is relevant to salon practice, addressing the need for reproducible regimens with controlled color durability, minimizing structural fiber wear, and reducing dermatological risks. The novelty lies in the integration of thermal profiling (DSC), morphology, and proteomic observations into a single process flowsheet tailored to the specific needs of the colorist. The work describes precursor diffusion pathways, chromophore formation reactions, and pH-controlled color fixation. The factors of washout, the role of acid stabilization, and the contribution of reconstructors such as "plex" are studied. Particular attention is paid to practical guidelines for selecting a developer, development time, and post-care. The goal is to build an evidence-based basis for selecting formulas for different initial hair conditions and scalp sensitivities. To achieve this, an analytical review, comparative analysis, and tabular aggregation of parameters were used. The conclusion provides recommendations for salon work and outlines safe pH ranges. This article will be useful for colorists, brand technologists, and teachers of practical trichology.*

Key words: *pH balance, permanent dyes, demi-permanent systems, acidic dyes, lightening, cuticle, melanin, DSC, bonders, dermatological safety.*

Introduction. Professional hair coloring relies on the controlled chemistry of swelling ion-active hair sites, dye diffusion, and the regulated degradation of natural pigment. Studio operations require harmonizing the depth and direction of the tone with the permissible alkaline load on the cuticle and cortex, as well as with scalp tolerability. Permanent systems offer the greatest freedom in shade construction due to alkaline activation and hydrogen peroxide H_2O_2; demi-permanent and acidic solutions maintain the surface in a denser state, reducing mechanical wear and enhancing procedural comfort. Concurrently, shade durability and leaching rates are determined by the pH balance before and after coloring, the selection of binding polymers, and maintenance regimes.

The aim of this study is to form an evidence base for selecting coloring/lightening formulas and regimes, taking into account the pH-dependent properties of hair and the scalp. The objectives are as follows:

1. describe the influence of pH on matrix thermal stability, cuticle permeability, and the kinetics of chromophore synthesis/fixation;
2. compare permanent, demi-permanent, and acidic formulas regarding color durability, leaching, and structural changes to the fiber;
3. systematize protection measures for the fiber and scalp, including acidic stabilization, reconstructors/bonders, and the correct selection of oxidizer and exposure time.

The scientific novelty lies in the proposal of a pH-oriented technological scheme that integrates DSC profiles, morphology, proteomic signals, and practical metrics (leaching, tribology) into a format of direct salon solutions without compromising scientific rigor.

Materials and Methods. The review is based on publications from recent years covering proteomic shifts, thermal degradation profiles, ingredient toxicology, post-bleaching morphology, leaching assessment methodologies, and clinical observations on tolerability. S.S. Adav [1] investigated pH-induced changes in hair structure and proteome; S. Breakspear, B. Nöcker, and C. Popescu [2] summarized the chemistry of interchain bonds and fiber behavior; T. Davies et al. [3] described DSC profiles under varying acidity levels; J.C. de Souza et al. [4] presented a consolidated classification of dyes, mechanisms, and toxicology; Z.D. Draelos [5] conducted a clinical evaluation of a permanent formula for sensitive skin; L. He et al. [6] examined the risks of coloring system ingredients; K. Hetherington et al. [7] proposed a method for quantitative pigment desorption from the fiber; D.H. Kim et al. [8] performed a comparative analysis of external and internal microstructure after intensive lightening; E. Martins et al. [9] validated a bleaching standard for testing reconstructors/bonders; V. Palaniappan et al. [10] systematized dermatological reactions during coloring.

The methodological framework includes an analytical literature review, the comparative method, content analysis of formula and regime descriptions, interpretation of thermograms based on published DSC data, and tabular aggregation of pH regimes and clinical outcomes.

Results. Cuticular scales, the endo- and exocuticle, the lipid cement of 18-methyleicosanoic acid, and cortical macrofibrils form a multilayered system sensitive to H^+/OH^- ion activity. Acidification increases the proportion of protonated sites in the matrix of keratin-associated proteins, reduces electrostatic repulsion, and decreases aqueous swelling; conversely, alkalinization accelerates hydration, intensifies the negative charge on the surface, and facilitates reagent diffusion into the cortex [3; 6]. Differential scanning calorimetry (DSC) of hydrated samples records a linear increase in the matrix denaturation temperature T_D as H^+ content increases into the strong acid zone, and a complex nonlinear pattern under excess OH^-, including abrupt changes around pH~12 due to cross-link rearrangement and potential lanthionine formation [3]. This dependency reflects a direct link between matrix cross-link density and fiber thermal stability; specifically, acidic environments strengthen interchain interactions, whereas alkaline environments facilitate the dissociation of solvent-sensitive bonds and cuticle opening [2; 3].

Oxidative dyes are built on reactions of primary and secondary aromatic amines/diamines with couplers under the action of hydrogen peroxide; pigment oligomers form within the shaft, parallel to the partial bleaching of melanin. Reaction progression requires an alkaline environment (typically pH~9–11), ensuring cuticle swelling and accelerated precursor diffusion; however, this regime carries the risk of enhanced degradation of keratin disulfides to cysteic acid during repeated coloring/lightening cycles [4; 5; 9]. A review of ingredient chemistry and toxicology records consistent data on sensitization to para-phenylenediamine/p-toluenediamine, as well as dose-dependent scalp irritation under alkaline exposure [5]. Clinical evaluation of an ammonia-free permanent system (substituting NH_3 with monoethanolamine) demonstrated comparable coverage and acceptable tolerability in patients with sensitive skin; nevertheless, questions regarding the long-term fiber damage profile of MEA systems remain a subject of discussion in professional literature [4].

Morphology after intensive bleaching is characterized by a loss of cuticle continuity, longitudinal cracks, and cortex exposure; electron microscopy studies record numerous zones of scale detachment and micro-voids in the endocuticular layer, increasing roughness and subsequent sorption/desorption of low-molecular-weight components [7]. A representative laboratory bleaching protocol on European hair provides a reproducible platform for testing reconstructors and bonders; quantitative metrics (cysteic acid, mechanics, shine) consistently confirm increased damage with greater exposure and number of procedures [9]. Analysis of repeated coloring/lightening cycles in models controlling for morphology and mechanics indicates a cumulative nature of cuticle destruction and protein loss, consistent with DSC thermograms and the reduction of $T_D/\Delta H_D$ following alkaline stress (see Figure 1) [3; 8; 9].

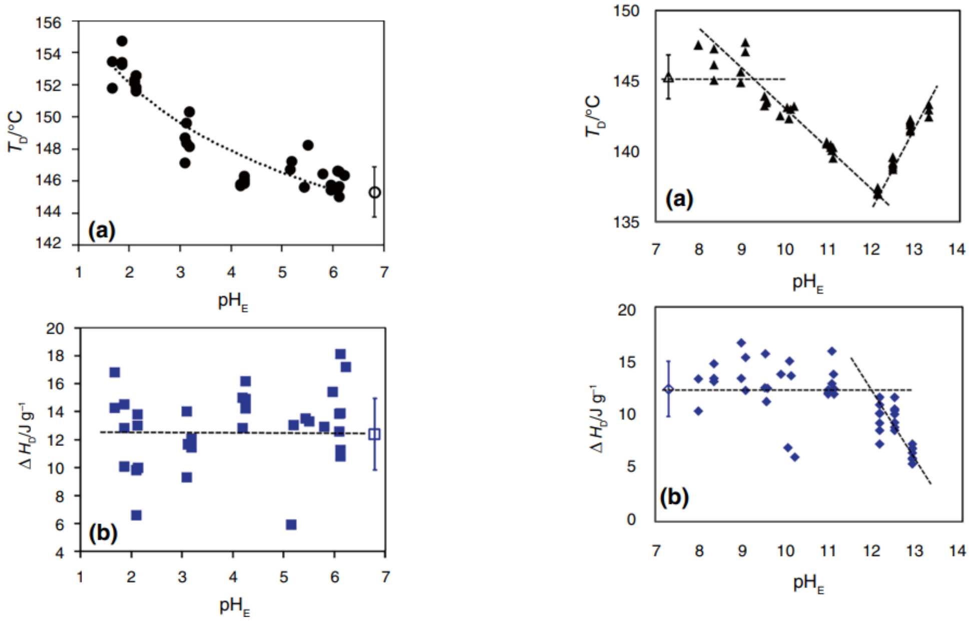

Fig. 1. Dependencies of matrix denaturation temperature T_D and enthalpy ΔH_D of human hair on pH after equilibration in acidic and alkaline environments according to DSC data [3]

The DSC curve in Figure 1 sets the framework for technological solutions: the rise in T_D and ΔH_D in the acidic zone indicates a densification of matrix interchain contacts; "dips" at high pH are associated with hydration and the weakening of ionic/hydrogen bonds. For permanent coloring, this implies that exposure time and oxidizer concentration should be rationally selected with regard to the minimally sufficient alkaline interval ensuring precursor diffusion into the cortex without excessive cuticle destruction. Selecting higher pH levels and H_2O_2 fractions accelerates chromophore formation but intensifies cysteic acid accumulation during repeated cycles. For demi-permanent and acidic systems, the priority shifts to color fixation via electrostatic and hydrophobic contacts at a weakly acidic pH, reducing swelling and tribological losses post-procedure.

Acidic and demi-permanent formulas are oriented toward depositing cationic/nitrodiazo and other direct dyes at weakly acidic pH values; cuticular swelling is limited, and fixation occurs primarily through ionic and hydrophobic interactions with the matrix. Comprehensive reviews indicate shallower penetration and better preservation of the protein scaffold compared to permanent systems, with an expected reduction in resistance to repeated washing [4; 6]. Leaching/desorption studies offer quantitative methodologies for comparing the tendency of pigment systems to exit the fiber; lower pH and a compacted cuticle reduce desorption, whereas alkaline stages and damaged cuticular architecture accelerate color loss [6].

The scalp reacts to alkaline compositions with itching, burning, and erythema; irritation escalation depends on peroxide concentration, contact duration, and total alkaline load. Dermatological reviews describe a spectrum of reactions—from irritative states to allergic contact dermatitis caused by precursors/couplers; the recommendation to shift post-procedural care to the acidic zone reduces subjective complaints and accelerates barrier recovery [5; 10]. Clinical series on ammonia-free formulas demonstrate a better sensory profile (odor, tingling) without compromising cosmeceutical outcomes in sensitive patients, while controlled acidic stabilization after coloring reduces inter-fiber friction and limits pigment loss during initial washes [4; 10].

Molecular mechanisms of pH influence are traceable through sets of thermal degradation and proteomic markers. Varying acidity reveals shifts in keratin and KAP-protein composition, and the ratio of oxidized forms of sulfur-containing amino acids changes; proteomic maps confirm structural dependence on ionic content and ionic strength of the medium [1]. At the macro level, this is expressed in changes to elastic moduli, viscoelastic characteristics, and swelling/shrinkage kinetics described in the review of interchain bonds, which emphasizes the sensitivity of hydrogen and ionic contacts to pH [2]. At the level of applied formulas, this picture explains why permanent systems utilize alkaline activators (cuticle opening and accelerated diffusion), while care products and acidic dyes stabilize the cuticle and minimize secondary degradation [2; 4].

Modern "plex" type additives (sulfo-/dicarboxylic acids, maleic/succinic derivatives, and patented oligopeptide motifs) are oriented toward reducing cysteic bond loss during alkaline stages and temporarily reorganizing the matrix. Validation schemes on standardized bleached strands show partial recovery of strength and shine indicators, as well as a reduction in cysteic acid content; however, this refers to damage compensation rather than a complete reversible "repair" of disulfides [9]. Integrating proteins, amino acids, and cationic polymers with acidic post-care additionally compacts the cuticle, increasing color fastness by reducing pigment desorption [6; 9].

Color dynamics observed during repeated procedures are determined not only by in-fiber pigment synthesis but also by the subsequent swelling-shrinkage balance during home care. Leaching studies show that the higher the proportion of alkaline stages and the stronger the structural damage after lightening, the faster the chromophore concentration in near-surface layers drops, and the higher the contribution of mechanical factors (friction, combing) to shine loss [6; 7; 8]. Lowering pH in post-treatment is a reliable tool to reduce discoloration rates during washing, consistent with calorimetric and morphological data [3; 6; 7].

In professional practice, selecting a coloring scheme reduces to balancing three blocks: the required tone depth/direction, the permissible alkaline load on the cuticle/cortex, and the post-procedural acidification strategy. Permanent formulas provide maximum tone plasticity and coverage due to alkaline activators and higher peroxide concentrations; the risk of cysteic acid accumulation and micro-cracks requires mandatory acidic stabilization and the inclusion of reconstructors according to standardized regimes [3; 7; 9]. Demi-permanent and acidic systems are preferable for toning and working with porous strands where cuticle preservation is critical; reducing pH decreases swelling and friction, improving tactile and tribological indicators without aggressive matrix modification.

Discussion. Comparing data on thermal stability and proteomic shifts under varying acidity indicates a bidirectional pH influence: moderately acidic conditions increase the cortical matrix denaturation temperature and interchain interaction density, whereas alkaline environments intensify hydration, cause swelling, and accelerate dye precursor diffusion deep into the shaft [1; 3]. Proteomic maps record pH-dependent changes in keratin and KAP-protein composition, consistent with the increase in oxidized sulfur-containing fragments under alkaline exposure and partial recovery upon acidification in post-care [1]. Thermal analysis of hydrated samples confirms nonlinear dynamics of T_D and ΔH_D over a wide acidity range, correlating with tribology observed by practitioners: a tight cuticle at low pH reduces friction and maintains shine, while alkaline stress facilitates micro-crack formation [3].

The chemistry of permanent systems explains shade stability and coverage through two coupled reaction lines: partial melanin bleaching by peroxide and intra-fiber synthesis of oligomeric chromophores from primary intermediates and couplers at a pH of approximately 9–11 [4; 6]. The shift toward ammonia-free schemes (substituting NH_3 with MEA and analogs) reduces the sensory load on the scalp and the severity of unpleasant odor without losing coverage in clinical series, but the long-term structural preservation profile of the fiber with MEA formulas requires careful interpretation, as the alkaline load on the cuticle persists [4; 5]. For studio application, this implies a choice between deeper cortex modification followed by mandatory acidification and toning regimes where color is fixed primarily by ionic and hydrophobic interactions in the weakly acidic zone [2; 4; 6].

A tabular summary of pH regimes is useful for making technological decisions in the salon. In the permanent branch, it is necessary to consider not only the mixture pH but also the H_2O_2 concentration, since bleaching speed and precursor penetration depth increase synchronously with rising alkaline and oxidative loads; in demi-permanent and acidic systems, the picture is reversed: limited swelling and lower diffusion increase cuticle preservation but decrease resistance to repeated washing [2; 3; 4; 6]. These relationships are summarized in Table 1; it presents working acidity intervals and expected technological outcomes confirmed by physicochemical and clinical publications [2–4; 6].

Table 1

pH Ranges and Typical Technological Outcomes in Coloring Systems [2; 3; 4; 6]

Dye Category	Typical pH Interval	Cuticle Diffusion/ Swelling	Color Fixation Mechanism	Expected Wash Fastness	Scalp Tolerability
Permanent (Oxidative)	9–11	High	Intra-fiber synthesis of oligomeric pigments	High with correct neutralization	Limited; higher irritation risk
Demi-permanent	6–7.5	Moderate	Partial intra-fiber capture + surface interactions	Medium	Higher compared to permanent
Acidic/Direct	3.5–6	Low	Ionic/hydrophobic bonds with matrix	Lower, higher sensitivity to shampoos	Favorable for sensitive skin

Comparison of morphology and mechanics after intensive lightening clarifies the limits of permissible alkaline load. Electron microscopy records loss of cuticle continuity, longitudinal cracks, micro-voids in the endocuticle, and loosening of the near-surface matrix; such zones act as entry windows for water and surfactants, accelerating dye desorption from near-surface layers [8]. Standard laboratory bleaching protocols proposed for calibrating reconstructor tests achieve a reproducible damage level suitable for comparing restorative effects regarding shine, roughness, and chemical markers [9]. The methodology for quantitative assessment of dye leaching tendency, based on desorption tests on fibers, adds a measurable index suitable for objectifying the impact of post-care pH strategies and binding polymer selection [7].

In clinical observations regarding ammonia-free permanent schemes in sensitive patients, acceptable coverage and a milder sensory profile (odor, tingling) are registered, while maintaining the need for strict control of exposure time and mandatory acidification after rinsing off the dye [5]. Dermatological reviews emphasize that sensitization risks to para-phenylenediamine and other intermediates persist regardless of the choice of the main alkaline agent; reducing scalp exposure through correct application, barrier creams, and care in the acidic zone decreases subjective complaints and irritation frequency [6; 10]. For the stylist, the priority remains a combined strategy: minimally sufficient alkaline load to achieve the target lightening level and a toning block in the acidic zone with cationic polymers and conditioning components [2; 4; 6; 10].

The issue of "plex" restorative additives and protein-amino acid systems requires terminology differentiation. Validation tests on standardized bleached strands show partial improvement in shine and mechanics, a decrease in oxidized sulfur-containing markers, and better combability; the result is interpreted as compensation and redistribution of bonds in the matrix, not as a direct return of disulfides to the initial state [9]. Transitioning to acidic stabilization after rinsing reduces swelling and decreases desorption flows, consistent with DSC thermograms for acid-equilibrated samples [3; 9]. To assess "long-term" shade durability, it is useful to incorporate desorption indices from quantitative leaching methodologies, as they provide a sensitive response to variations in post-care and binding polymer type [7; 9].

Tabular integration of damage and color retention metrics facilitates strategy comparison. Table 2 summarizes benchmarks for morphology, thermal stability, and leaching kinetics under three regimes: "lightening without reconstructor," "lightening with reconstructor/bonder," and "toning in the acidic zone."

Table 2

Fiber Damage and Color Retention Under Different pH Strategies [3; 7–9]

Regime	Cuticle Morphology	Matrix Thermal Stability (DSC)	Damage Indicators	Pigment Desorption Tendency
Lightening without reconstructor	Numerous detachments, longitudinal cracks	Decrease in T_D and ΔH_D after alkaline exposure [3]	Increase in oxidized sulfur markers; loss of shine	Higher compared to toning; accelerated leaching
Lightening with reconstructor/bonder	Reduced detachment severity, smoother scale edges	Partial return of $T_D$profile to pre-treatment values [3; 9]	Improvement in shine/combability; partial reduction of oxidation markers	Lower than without reconstructor; depends on binding polymers
Toning in the acidic zone	Intact or compacted cuticle	T_D stable or higher compared to alkaline regime	Minimal structural changes compared to initial state	Lower with proper post-care; sensitivity to frequent shampooing remains

The practical implication for palettes and oxidizer selection is that for target tasks associated with neutralizing a dominant warm undertone after strong lightening, it is rational to combine limited alkaline exposure with subsequent acidification and the use of binding polymers that reduce desorption. When working with porous and previously lightened strands, preference shifts to acidic toning formulas with cationic dyes, where fiber structural preservation is higher, and corrective procedures are performed more frequently due to lower wash fastness [2–4; 6; 7; 9]. In cases of sensitive scalp, clinical observations indicate a reduction in subjective reactions with ammonia-free systems, although control of allergens such as para-phenylenediamine remains an immutable requirement for consultation and patch testing [5; 10].

For studios, technology is selected based on two limiting conditions: the required depth of lightening/undertone neutralization and the maximum permissible alkaline load, taking the client's hair history into account. Tone-on-tone and slight darkening are more rationally addressed in the weakly acidic zone with a priority on cationic dyes, conditioning components, and acidic rinse stabilization. Deep color transformations require a permanent block with dosed H_2O_2 and the inclusion of reconstructors at pre/post-exposure stages; control of time and temperature is critical to prevent excessive disulfide degradation.

Conclusion. pH determines cuticle permeability, matrix thermal stability, and chromophore formation rates, which is reflected in shade durability and the level of structural wear. Permanent alkaline systems offer maximum color variability provided there is dosed H_2O_2, strict time control, and a mandatory transition to acidic stabilization after rinsing. Demi-permanent and acidic solutions are preferable for porous and previously lightened strands: limited swelling reduces tribological losses and maintains the surface in a denser state with moderate durability. Reconstructors/bonders reduce the severity of alkaline damage and improve combability but do not replace a correct pH strategy and oxidizer selection. For studio practice, it is advisable to rely on a pH matrix of regimes, utilize acidic post-care, and employ validated color leaching assessment methodologies; such a scheme increases result reproducibility, reduces the frequency of scalp irritations, and sets stable quality for toning and lightening tailored to individual client goals.

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