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Studying the Effect of Optical Aging by Transitional Elements on Yellowness Property of Newsprint Paper

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Abstract: Metal ions present in chemimechanical pulps lose their brightness upon reaction with lignin of the paper fiber while some of their properties will be increased including yellowness. The objective of this study was to evaluate and determine the amount of variation in yellowness characteristics of chemimechanical papers which were produced in Mazandaran Wood and Paper Company through treatment with some transitional metal ions in addition to relevant techniques to decrease it. Yellowness in pulps produced through mechanical or chemimechanical procedures are desirable due to study their aging content and other brightness parameters related to them as well. Some samples of paper in unbleached mode were prepared from the factory and then, they were treated using two following chemical materials. Firstly, they were wetted using chelating agent of EDTA (Ethylene Diamine Tetraacetic Acid) in various concentration levels. This process will neutralize available ions in samples of CMP (Chemimechanical papers) and the available metal ions which trigger aging and yellowness regimes, will be Neutralized. Secondly, when wetted samples with EDTA are dried, they are wetted again by solutions containing transitional element ions. Results revealed that the most prevalent effect on yellowness improvement was associated with Fe_2^+ ions while the least considerable one was related to ions of Al_3^+. Al_3^+ similar to a neutral ion did not show a significant effect on increasing the yellowness. Besides, when samples are wetted using different EDTA concentrations, there will be a significant decrease in detrimental effects which decrease brightness and increase yellowness contents. In order to improve brightness parameters and prevent unfavorable characteristics such as yellowness, some techniques have been proposed namely methylation [1] and removing yellowness making elements (Kenones) [2].

Key words: Hardwood CMP · Transitional metal ions · EDTA · Yellowness · Accelerated optical aging

INTRODUCTION

Increasing the durability without causing negative effects on brightness, physical properties and strength of CMPs is one of the main targets of manufacturing companies. Since some of the paper consumed in Iran is produced by chemimechanical process, it is important to consider optical properties as well as solutions to decrease yellowness and aging effects. Ions of transitional element such as Fe_2^+, Cu_2^+ and Mn_2^+ cause paper to be colored [3]. The affinity of ions from transitional elements to react with lignin and formation of colorful complexes in samples which are produced from lignin containing species is more than species which have less lignin contents. Several methods have been considered to decrease negative effect of the ions one of which is using chelating agents [4]. Since chelating materials employed in the previous experiments such as DTPA (Diethylene Triamine Penta Acetate) are rather expensive, emphasis will be on considering inexpensive substitutes like EDTA. During a typical pulping process, water, equipments and even wood chips can act as sources of ions from transitional elements. In order to mitigate the negative effects of ions, using distilled water is not economically feasible. Thus, methods such as using chelating elements including EDTA, decreasing pulp's pH value [4] and other techniques like Acetylation [5] are proposed. Scientifically speaking, paper produced from chemimechanical pulp is composed of cellulose, hemi cellulose, lignin, extractive materials, additives, starch and starching materials, Filler materials and pigments. Mechanically produced and high yield pulps such as CMP which have a lot of lignin, decline in whiteness or well-known "yellowness" phenomenon will happen intrinsically in absence of light or in presence of light and UV waves in 300-400nm wavelengths with higher

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amplitudes. Researchers have shown that light induced coloring will be intensified by oxygen while humidity does not affect it much [6]. Carter (1996) by studying on colors of pulps containing great amounts of lignin argued that under light, heat, humidity, active ions such as Ca_2^+ and Fe_3^+ and gas Pollutants especially SO_2 and NO_2, yellowing will occur due to oxidation and photo-oxidation of chemical groups in paper in addition to creation of new colorful groups [3]. Monica *et al.* (1973) assess the light-induced yellowing mechanism of Acetylated pulps from GW (Ground Wood). The effect of partial Acetylation on light-induced yellowness of unbleached pulps, beached pulps with hydrogen peroxide and reduced by GW pulp's borohydride exhibited that the kenonic compounds in light-induced oxidized pulps before Acetylation have caused development in Chemical reactions [7]. Saint *et al.* (2002) evaluated using yellowness inhibitors in the mechanical pulps. In their research, kinetic stability and equilibrium of 2-benzotriazole, as yellowness inhibitor, was quantified by studying variations in type and density of the inhibitor and also concentration of the salt under study [8]. Qiu *et al.* (2003) focused on DTPA in order to decrease peroxide analysis with Mn ion. Effect of metal ions such as Mn_2^+ on the analysis behavior of hydrogen peroxide using DTPA as inhibitor was assessed. The results indicated that adding DTPA to pulp containing Mn_2^+ was more effective that the pulp without DTPA addition [9]. Mirshokraei (2005), has launched to study the effect of metallic ions on optical properties of CMP which was prepared from hardwood species. DTPA was utilized as the chelating material in the experiment. In this regard, Pulp supplied from Mazandaran Wood and Paper Company was pre-treated with DTPA first. Then, it was bleached by hydrogen peroxide under specific conditions. After decreasing the pH values and bleaching, distilled water, water with metallic ions, tap water and industrially used water were selected to implement light-induced accelerated aging procedures on the hand-made paper samples. Based on observations and results of this test, the most detrimental effect on optical properties, yellowness and aging phenomena was pertained to the Fe_2^+ ion while the least detrimental effect was related to ions of Al_3^+. Furthermore, presence of chelating agent of DTPA caused brightness stability to be increased [4]. Veysi (2005) have studied coloring of steeled CMP pulps prepared from two species of beech by light-induced and heat-induced aging. obtained results were indicative of the fact that upon Acetylation, steel groups have simply replaced hydrogen in the lignin phenolic hydroxyl, there by blocked motion of the electrons in propane phenyl. Stability of brightness will be increased because light absorbing kenones are not formed [2].

Experimental: CMP pulp samples were supplied by Mazandaran Wood and Paper Company in unbleached mode. For better saturation and absorption, samples were prepared in smaller dimensions. Since some samples were wrinkled that may produce difficulties in measuring the optical properties of treatment, saturation method was used rather than spray. Generally speaking, samples were used in two forms: (1) Control sample (without any treatment), (2) Sample with EDTA treatment followed by treatment by solutions containing metallic ions.

In this section, ions present in CMP paper samples were neutralized after saturation with EDTA chelating agents. After being dried, samples were exposed to saturation with each one of the solutions incorporating Metallic ions.

Research background refers back much to employing DTPA chelating agent. Concentration of this material in the production line of Mazandaran Wood and Paper Company is approximately 0.3%. EDTA chelating agent has been used with various concentrations in experiments. But the optimal concentration of EDTA in decreasing the detrimental effect of ions is 0.5%. In this study, EDTA chelating agent has been employed to assess its usage and substitution by DTPA regarding its lower price. The effect of EDTA was evaluated in 0, 0.25, 0.5, 0.75 and 1% concentration levels. In order to make EDTA containing solution and prevent error creation in test results and negative effect of ions present in the tap water, Deionized water was used rather.

pH value of the EDTA solution was set to 5.5 to 6.

In order to make solutions which contain metallic ions of transitional elements, using salts of metallic ions soluble in water such as nitrates and sulfates had significant importance. In order to prepare solutions with metallic ions, deionized water was used to stop harmful ions entering drinking water and industrial water. "How much effective is each one of the metallic ions?" is answered by amount of their concentration in the consumed water of factory. Following salts are used to produce solutions which contain metallic ions:

$FeSO_4.7H_2O$-$CuSO_4.5H_2O$-$MnSO_4.H_2O$-$FeCl_3.6H_2O$-$AlCl_3.5H_2O$

The concentrations of these ions are determined based on their common values in the water consumed by the factory as below:

Fe_3^+	Fe_2^+	Cu_2^+	Al_3^+	Mn_2^+
1 ppm	0.3 ppm	0.1 ppm	25 ppm	1 ppm

Table 1: Data related to the yellowness characteristics of CMP paper samples in different times and concentrations of EDTA and metallic ions

Ion Concentration	EDTA%	0 hours	10 hours	20 hours	30 hours	40 hours	50 hours
0.3ppm Fe_2^+	0	10.17	13.81	15.76	18.49	21.70	22.55
	0.25	10.02	13.70	15.21	18.31	21.45	22.11
	0.5	9.83	13.49	14.93	18.01	21.15	21.86
	0.75	9.83	13.39	14.52	17.63	20.87	21.15
	1	9.69	13.01	14.51	16.90	21.02	21.39
1ppm Fe_3^+	0	9.88	12.41	15.21	18.11	20.86	21.79
	0.25	9.71	12.30	15.11	17.85	19.93	21.15
	0.5	9.61	12.30	14.89	17.39	18.86	21.02
	0.75	9.52	11.89	14.21	17.11	19.06	21.12
	1	9.53	12.05	14.31	17.21	18.92	20.89
0.1ppm Cu_2^+	0	9.70	12.21	14.83	17.76	20.12	20.84
	0.25	9.53	11.83	14.29	17.49	19.86	20.70
	0.5	9.46	11.76	13.39	17.21	19.21	20.49
	0.75	9.21	11.80	13.70	18.11	18.89	20.83
	1	8.93	11.80	13.41	17.79	18.83	21.01
1ppm Mn_2^+	0	9.45	12.06	14.76	17.23	19.71	20.53
	0.25	9.31	11.65	14.05	17.25	19.45	20.61
	0.5	8.89	11.41	13.21	17.01	18.86	20.31
	0.75	8.79	10.90	12.89	18.13	14.49	20.66
	1	8.85	10.91	12.73	17.86	18.21	20.44
25ppm Al_3^+	0	9.40	11.86	12.92	13.21	15.86	17.46
	0.25	9.41	11.42	13.71	13.89	16.29	17.73
	0.5	9.11	11.20	13.17	14.29	16.80	17.65
	0.75	8.66	40.49	12.83	16.51	17.81	17.95
	1	8.67	10.39	13.21	15.11	17.21	17.96

Drying the samples was done in an environment without light and moisture, since paper samples were prone to absorb optical waves and yellowing as they were saturated with EDTA and metallic ions. Mild fan blowing was used to dry samples in the abovementioned conditions. A simulated apparatus was used for accelerated light induced aging experiments. 6 UV lamps of Black Light made by Philips were used in addition to 4 regular fluorescent lamps. The output frequency had a range of 300 to 400nm. Light induced treatments were implemented in time spans of 0, 10, 20, 30, 40 and 50 hours. In order to measure brightness of paper, Technibrite Micro TB-1C Spectrophotometer apparatus was Utilized. All measurements were done on the basis of Tappi-T452-OM-98 standard.

Data analysis was directed by SPSS software, while multi-domain test of Duncan was used for separating average values and studying individual and mutual effect of each variable.

Table 1 summarizes data related to yellowness characteristics versus variables of time, EDTA concentration and metallic ions in the bleached CMP samples. Increase in time duration will always raise the yellowness content and indeed the aging number. This regime is repeated for all ions and EDTA concentration values. Higher concentrations of EDTA will cause yellowness index to be increased with lower ratios. In fact this is the chelating agent that raises the brightness stability and improves the brightness properties. Table1 reveals that the most effective ion on increasing the yellowness is Fe_2^+, while Al_3^+ acts as the least effective one.

Table 2 has summarized multi-directional variance analysis for the yellowness characteristics of unbleached CMP samples versus time, concentration of EDTA and metallic ions which act as different variables. All variable parameters had a meaningful impact on the yellowness content and each of them was able to change that value meaningfully.

During the study on mutual effect of each variable in Table 2 it can be seen that the effect of each variable on other variable has also been meaningful. Evaluation of the Mutual effect of ion-EDTA shows that the increase in the concentration of this chelating agent, regardless of

Table 2: Multi-directional variance analysis for yellowness characteristics of CMP samples versus variables of time, EDTA and metallic ion concentrations

Source of Variation	Squared Sum	Degree of Freedom	Squared Average	F statistic	P value
Ion	412.526	4	103.1320	1031316.300	0.000
EDTA	22.487	4	5.6220	56218.680	0.000
Time	6791.464	5	1358.2930	13582927.472	0.000
Ion-EDTA mutual	13.583	16	0.8490	8489.630	0.000
Ion-time mutual	133.899	20	6.6950	66949.422	0.000
Time-EDTA mutual	14.035	20	0.7020	7017.432	0.000
Ion-time-EDTA mutual	33.549	80	0.4190	4193.582	0.000
Error	0.030	300	0.0001		
Total	7421.573	449			

Table 3: Duncan test results for studying the effect of ion variable on the yellowness characteristics of unbleached samples

		Subgroups				
Ion	quantity	1	2	3	4	5
Al_3^+	90	13.6563				
Mn_2^+	90		15.1537			
Cu_2^+	90			15.5153		
Fe_3^+	90				15.8067	
Fe_2^+	90					16.5507
P value	Sig	1.000	1.000	1.000	1.000	1.000

the effect of metallic ions on raising yellowness properties, has been able to meaningfully improve and stabilize the brightness properties as well. Although there has been some impact from metallic ions on increasing the yellowness characteristics (Fe_2^+ being the most and Al_3^+ being the least effective ions), EDTA has enhanced the stability of brightness. Meanwhile considering the impact of each ion on yellowness variations, EDTA has caused yellowness to be increased with much less intensity. Besides, studying the mutual effect of the two variables of ions and time shows that the time has always been able to increase the yellowing meaningfully. In other words, time lapse for the Fe_2^+ ion which had the most prevalent impact on yellowness, has decreased the brightness while increased the yellowness characteristics. Time lapse has also increased yellowness for the neutral ion of Al_3^+. Emphasis on the mutual effect of the two variables of time and EDTA exhibited that however the time lapse has yielded higher yellowness; increase in the EDTA caused yellowness to be increased in light-induced aging times with lower ratios. It means that the EDTA increase has noticeably improved brightness properties for all aging times.

Since all three elements have been effective in accordance to table 2, this question may be put forward that "Are all different variable levels effective on decreasing the brightness or not?" Based on table 3 it can be observed that for evaluating effective variables of metallic ions on the yellowness content of the unbleached CMP samples in Duncan test, the most significant effect in increasing yellowness, decreasing brightness, brightness stability and quality of brightness properties is associated with Fe_2^+ ion, while the least significant of them is associated with ion of Al_3^+. These results agree well with those offered in table1. In other words, average values of the yellowness characteristics are in a meaningful level for all ions. Ni *et al.* (1998) have concluded that the Fe_2^+ can be simply oxidized into Fe_3^+ and their bleaching potential can be enhanced [10]. Then, Fe_3^+ ion will have the ability to change yellowness characteristics meaningfully [11].

Figure 1 depicts effect of time and EDTA concentration on increasing yellowness characteristics of the unbleached samples which were saturated by Fe_3^+ ions. It is clear that curves associated with lower concentration EDTA are placed in higher levels. Level of curves descends as the EDTA concentration increases and it includes lower yellowness changes which are increased with much less ratios.

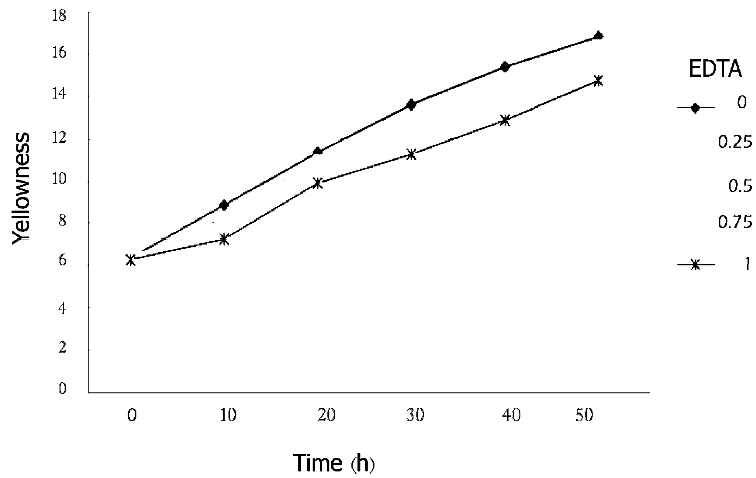


Fig. 1: Effect of time and EDTA concentration on the yellowness characteristics of samples saturated with Fe_3^+

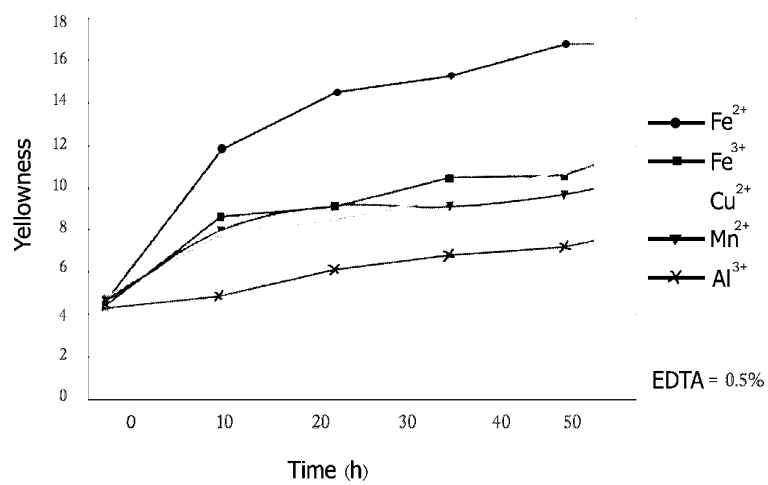


Fig. 2: The effect of transitional ions on the yellowness characteristics of unbleached samples

Table 4: Duncan test results for studying the effect of EDTA Variable on the yellowness characteristics of unbleached samples

		Subgroups				
EDTA	Quantity	1	2	3	4	5
1	90	15.0920				
0.75	90		15.1620			
0.5	90			15.2413		
0.25	90				15.4980	
0	90					15.6893
P value		1.000	1.000	1.000	1.000	1.000

Table 4: Duncan test results for studying the effect of time variable on the yellowness characteristics of unbleached samples

		Subgroups					
Time	Quantity	1	2	3	4	5	6
0	75	9.4064					
10	75		12.0016				
20	75			14.0920			
30	75				16.9928		
40	75					19.1380	
50	75						20.3884
Sig		1.000	1.000	1.000	1.000	1.000	1.000

In studying the different contents of chelating agent of EDTA which has been nominated as Duncan test in table4 with the objective of studying EDTA variable parameter on yellowness properties of the unbleached CMP, similar to its effect on enhancement of the brightness properties, it is obvious that concentrations up to 1% are able to impose meaningful changes on improvement of the yellowness index. Although the optimal range of using chelating agents is 0.5% and its more usage can cause some improvements in the brightness properties, it is not feasible economically.

Table 5 includes the results obtained for Duncan test in studying the effect of time variable on yellowness characteristics of unbleached CMP samples. This table indicates that the increase in time from 0 to 50 hours will develop meaningful changes on yellowness content.

Generally speaking, yellowness contents of the unbleached CMP samples introduce Fe_2^+ and Al_3^+ as the most effective and least effective ions, respectively. This was in accordance with the results reported by other researchers (based on table3) [4]. $Al_3^+ < Mn_2^+ < Cu_2^+ < Fe_3^+ < Fe_2^+$

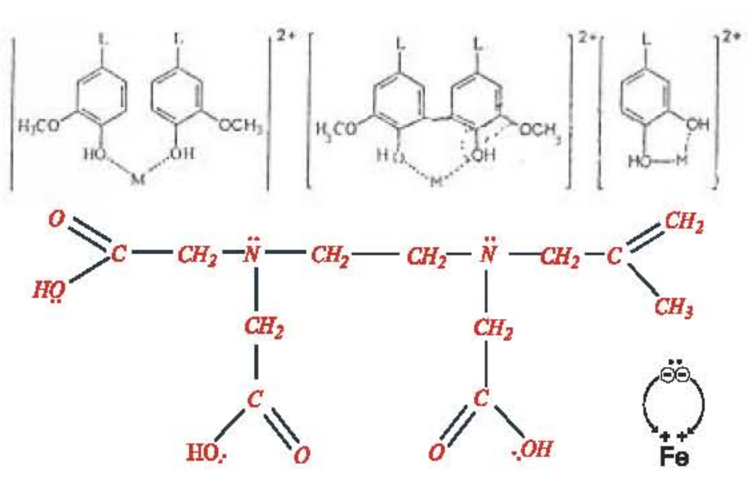
CONCLUSIONS

Yellowness is nominated as the amount of difference between light emission and whiteness in percentage and also as the measure for getting far from whiteness. Several arbitrary factors participate in high yield pulps such as: oxygen, α-carbonyl structure, binary bonds of lignin, free oxygen, free radicals, several types of peroxides, phenollic groups (i.e.cathecole), orthokenones, parakenones (i.e. metoxi-p-benzokenone), β-0-4 lignin, hydro kenones and Acetylene created from comaran phenyl12. Researches show that Acetylene exist in high yield and unbleached pulps with peroxies. Furthermore, active oxygen containing compounds such as hydroxyl radical (HO°), hydroperoxyl radical (H_2O°), alchoxy radical (RO°), alkyl proxy radical (RO_2°), anionic radical (O^-2°), oxygen groups ($3O_2$), oxygen (O_2), oxygen atoms of O° (from ozone) and hydrogen peroxide (H_2O_2) are examples of chemical compounds which are the reason for part of oxidation process. Cellulose and lignin chromophores are known as the yellowing agents in paper [13].

Cellulose is a saccharide homopole in Which anhydrous cellubiose units are repeated (1.03nm). Tshriner *et al.* (1998) have stated that carbonyl and carboxyl groups have been formed from anhydrous glucose units upon oxidation or photo-oxidation [14]. Saint *et al.* (2002) have designated oxidized hemicelluloses chromophores as aldehyde groups on C2 and C3 carbon atoms. Lignin is and aromatic polymer which is composed of Propane phenyl units and etheric bonds exist in its structure with lower C-C bonds [8]. Monika *et al.* (1991) have stated that the contributions of oxidized cellulose and hemicelluloses yield the minimum yellowness in lignin containing papers, since the contribution of coloring lignin groups are much significant than cellulose and hemi cellulose [6]. Abdul Khalil *et al.* (2005) have argued that due to the photo-oxidation behavior of lignin, aromatic ketones, kenones, aldehydes and acids will be produced [12]. Formation mechanism of chromophores and lignin destruction upon yellowing and lignin's photo-oxidation is explained below:

Primary chromophores of lignin: light Absorption with 300 to 400nm wavelengths-break of etheric bonds and creation of free radicals-reaction between the free radicals and lignin-formation of ketyl radical-phenoxy and ketone radical-production of yellow kenones and chromophores with secondary chromophores-light-induced destruction of lignin and paper's yellowing [2].

The general structure of lignin and metallic complexes is schematically sketched in the following: Where M2 is the metallic ion:



Thus, all oxygen electron pairs will chelate metallic ions and surround them in other words. So they would not let them form stable complex with lignin which may cause optical damages to lignin and yellowness of paper. Observing the statistics obtained for yellowness content of bleached and unbleached samples implies that the parameter of time has also played a key role in modifying the yellowness characteristics. Thus, results were indicative of a meaningful effect of time on the yellowness characteristics. In other words, increasing the time duration has raised these characteristics significantly. On the other hand, yellowness properties has also been subjected to parameters such as ion type, Concentration of the chelating agent, time of light-induced aging and lignin content of the samples. Fe_2^+ has also provided the most impacts on yellowness characteristics as a completely effective and destructive ion. It has exerted more detrimental impacts due to formation of oxygen containing radicals in comparison with other ions which can be attributed to acceleration in creation of Phenoxy radicals by Fe_2^+ ions. Chelating agents such as EDTA apply a positive effect and cause yellowness characteristics to be increased in lower ratios when time elapses. Meanwhile, yellowness content will be increased a little versus accelerated light-induced aging time which can be attributed to the more reactive situation of EDTA in addition to the formation of stable constants with the metallic ions. In other words, chelating material such as DTPA and EDTA will confine the ion and will avoid its destructive function. Although using chelating materials is exposed to some limitations from scientific and economic points of view, it is not economic to use these materials in high content and higher concentrations. It is not possible to expect more effects when concentration values are increased. Because the optimal limitation of using this material is about 0.5% and its maximum usage is almost 1% above which no effect on yellowness improvement can be observed, while it is not economically feasible to utilize this material in high contents.

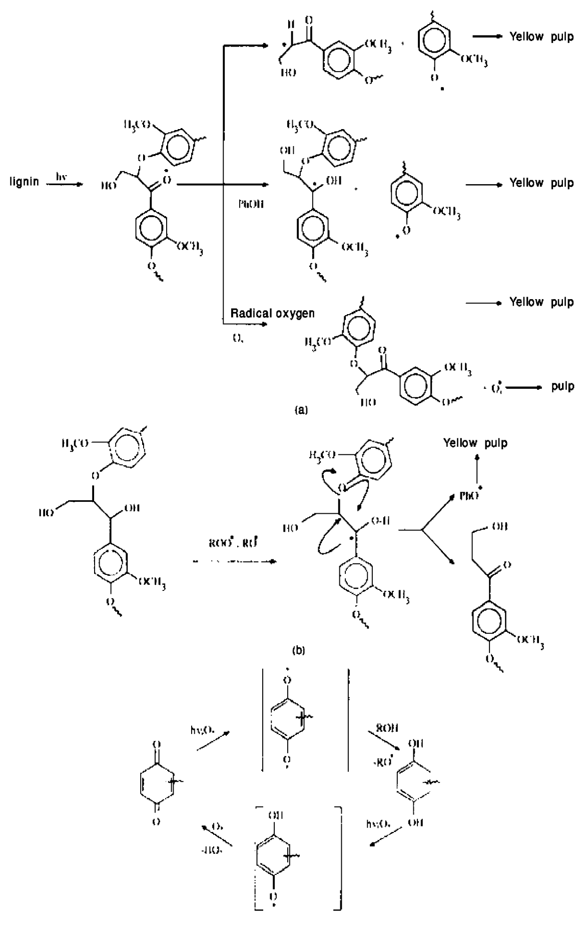


Fig. 3: Mechanism of yellowness in high yield pulps: (a) phenasyl reaction, (b) reaction of free ketyl radical and (c) oxidation-reduction cycle in yellowness process of paper [13].

The general mechanism of the chelating materials including DTPA, EDTA and DTPAMP is that metallic ions form very stable complexes with phenolic composition [5] whose stability constant is high. But chelating agents such as EDTA will create more stable constants with metallic ions due to their more reactive conditions. Therefore, ion-EDTA complexes will get more thermodynamic equilibrium when paper samples are saturated with EDTA and by increasing the concentration of EDTA, the effect of metallic ions will be reduced. Generally speaking, in unbleached samples which contain more lignin and extractive materials, the contribution of coloring lignin is much significant, since the role of oxidized cellulose and hemicelluloses is minimized in creating yellowness on the paper [1]. Some techniques such as modifying the primary chromophores, reduction by sodium borohydride [5], using chelating agents [4], employing inhibitor agents which prevent yellowness in the mechanical pulps (amine hydroxyl) [14], reduction in pH value of the pulp (due to lower durability of the metallic ions) [9], acetylation [6] and methylation [1] have been proposed as effective methods to enhance optical properties of the paper, increase in the brightness stability, prevention from yellowing or reducing its rate, light induced coloring or aging of CMPs.

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