

CHAPTER V

COMPLEX FORMATION IN CROSS-LINKING OF CELLULOSE

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In recent years various research groups have reported highly active catalysts for cross-linking cellulose with formaldehyde or amino-formaldehyde adducts^{1 - 4}. The highly active catalysts are formed from the combination of certain metal salts and organic acids, the catalytic activity of the mixture being greater than that of either component alone. The high activity of the mixed system has been attributed to complex formation between hydroxy acids such as citric or tartaric acid and the metal ion of the salt. In Chapter III it has been shown that even organic acids which do not contain hydroxy group also form such active mixtures. Apart from the complex formation between acids and metal salts, other complexes between metal salts and the resin and between metal salt and cellulose have also been suggested. It is yet not established which complex formation contributes predominantly in accelerating the cross-linking reaction. A short review of the literature regarding various complexes is given below.

Many complexes between salts of sodium, lithium, barium, calcium, strontium and iron, and molecules of carbohydrates are

known to exist^{5,6}. Richards et al⁷ reported complex formation between aqueous zinc chloride and D-glucopyranoside. They have shown that zinc chloride complexes with vicinal hydroxyl groups at C₂ and C₃ and at C₃ and C₄ of D-glucopyranoside ring. As the concentration of zinc chloride is increased, the concentration and stability of the complex increases reaching a maximum at 8 - 10 molar concentration of zinc chloride. The analogy between the formation of a complex with methyl β-D-glucopyranoside and the swelling and crystallinity behaviour of cellulose indicate that formation of a complex between cellulose and zinc chloride is probably involved in the swelling mechanism. Daruwalla et al⁸ have shown that cellulose and cellobiose form complexes with zinc chloride. Schwalbe et al^{9 - 11} reported catalytic action of cellulose on the thermal decomposition of metal salts such as zinc chloride and magnesium chloride with the liberation of hydrochloric acid. Belford et al¹² studied the sorption of metal ions by cellulose and suggested that the ions are adsorbed to form a regular two dimensional lattice on the surface of microfibrils by complex formation with hydroxyl groups of the cellulose molecules. Halpern et al¹³ have reported thermal decomposition of cellulose in the presence of neutral, acidic and basic additives. Some of their data are shown in Table IX.

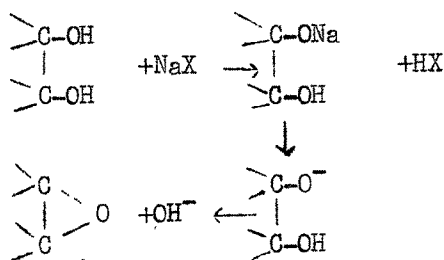
TABLE XX

ISOTHERMAL PYROLYSIS OF 1 g. OF COTTON FOR FIVE HOURS IN THE PRESENCE OF 10^{-4} MOLE OF VARIOUS ADDITIVES

	Additive	Weight loss mg.
250°C	None	62
	Na_2CO_3	355
	NaHCO_3	258
	NaCl	183
	LiCl	190
	NaHSO_4	226
	Na_2SO_4	73
275°C	None	493
	NaCl	546
	NaHSO_4	559

In case of LiCl and NaCl evolution of hydrogen chloride takes place. After heating 1 g. of cellulose with 10^{-4} moles of NaCl at 250°C for 1, 3 and 5 hours the aqueous fraction contained 0.25, 0.56 and 0.58×10^{-4} equivalent of chloride respectively. Similar results were obtained with lithium chloride and also with sodium bromide. With a neutral salt of a non volatile acid such as sodium

sulphate the weight losses obtained are very small possibly because the sulphuric acid formed by pyrolysis may be used up in sulphonation of cellulose. In case of volatile acids the following sequence of reactions involving hydroxyl group may occur:



The principal factor in the reaction may be the volatility of the acid produced. Lewin¹⁴ observed that the heating of cellulose with magnesium chloride resulted in decreased degree of polymerization of cellulose. This decreased D.P. is due to the hydrolysis of cellulose by the hydrochloric acid formed. Miller^{15,16} observed that the presence of metal chlorides and nitrates modify the thermal behaviour of cellulose and weight losses are observed at different temperatures depending upon the particular salt and its concentration. These weight losses are probably due to the formation of nitric and hydrochloric acids.

In short metal salts form complexes with cellulose and liberate inorganic acids. The acid formed will act as a catalyst for the reaction of cellulose with the cross-linking agents.

Complex formation between metal ion and cross-linking agents are reported by various workers. Haith et al¹⁷ suggested that complex formation of the Lewis acid in aqueous amidomethylol resin solution is possible between the carbonyl oxygen and the hydroxyl oxygen. Berni et al¹⁸⁻¹⁹ reported complex formation between N- of DMEU and the metal ion on the basis of infra-red spectra and the presence of metal in cross-linked cellulose. The complex formation between metal ion and organic acids is discussed in Chapter III. In the present work it has been found that the formation of a more stable salt of the organic acid and metal cation, and consequent liberation of strong volatile acid are responsible for the higher activity of the mixed catalysts. Further, it is found that on the basis of infra-red spectra and metal contents of the cellulose cross-linked with DMEU it is not possible to show conclusively that complex formation between DMEU and metal ion occurs.

RESULTS AND DISCUSSION

Berni et al¹⁹ published infra red spectra of the cellulose cross-linked with DMEU in the presence of latent acid type metal salts such as magnesium chloride, zinc chloride and zinc nitrate. They observed a shift of the $\text{C} = \text{O}$ band occurring at 5.95μ to slightly higher frequencies (5.89μ) representing a total shift

of 26 cm^{-1} from that of the $\text{>C} = \text{O}$ band occurring in DMEU crystal at 5.98μ . They attributed the observed shift of 26 cm^{-1} to the formation of nitrogen to metal bonds, that is to existence of a co-ordination complex between the DMEU and catalyst.

The infra-red spectra of the samples cross-linked with DMEU in the presence of different catalysts are shown in Fig. 36. Table XXI represents the position of carbonyl band. The carbonyl absorption peak of the samples (3) and (4) are similar. Similarity in the carbonyl absorption peak indicates that the carbonyl shift is due to cross-linking and is observed irrespective of the catalyst used.

Spectra of the samples (5 to 10) cross-linked with DMEU using oxalic acid as catalyst at various pH of the pad bath are shown in Fig. 36. Sample (5) shows a broad band at 6.10μ . The absence of a sharp carbonyl peak at 5.90μ is due to lower fixation of the resin at this pH. At pH 4.0, sample 6 a broad band appears at 5.90μ ; however, a slight shift towards higher frequency is observed. At pH 3.50 and below a sharp peak at 5.90μ is obtained. These spectra show that the absorbed water band at 6.10μ is slowly disappearing with the increase in fixation of resin and when the absorbed water band disappears completely, a sharp carbonyl peak at 5.90μ is observed.

TABLE XXI

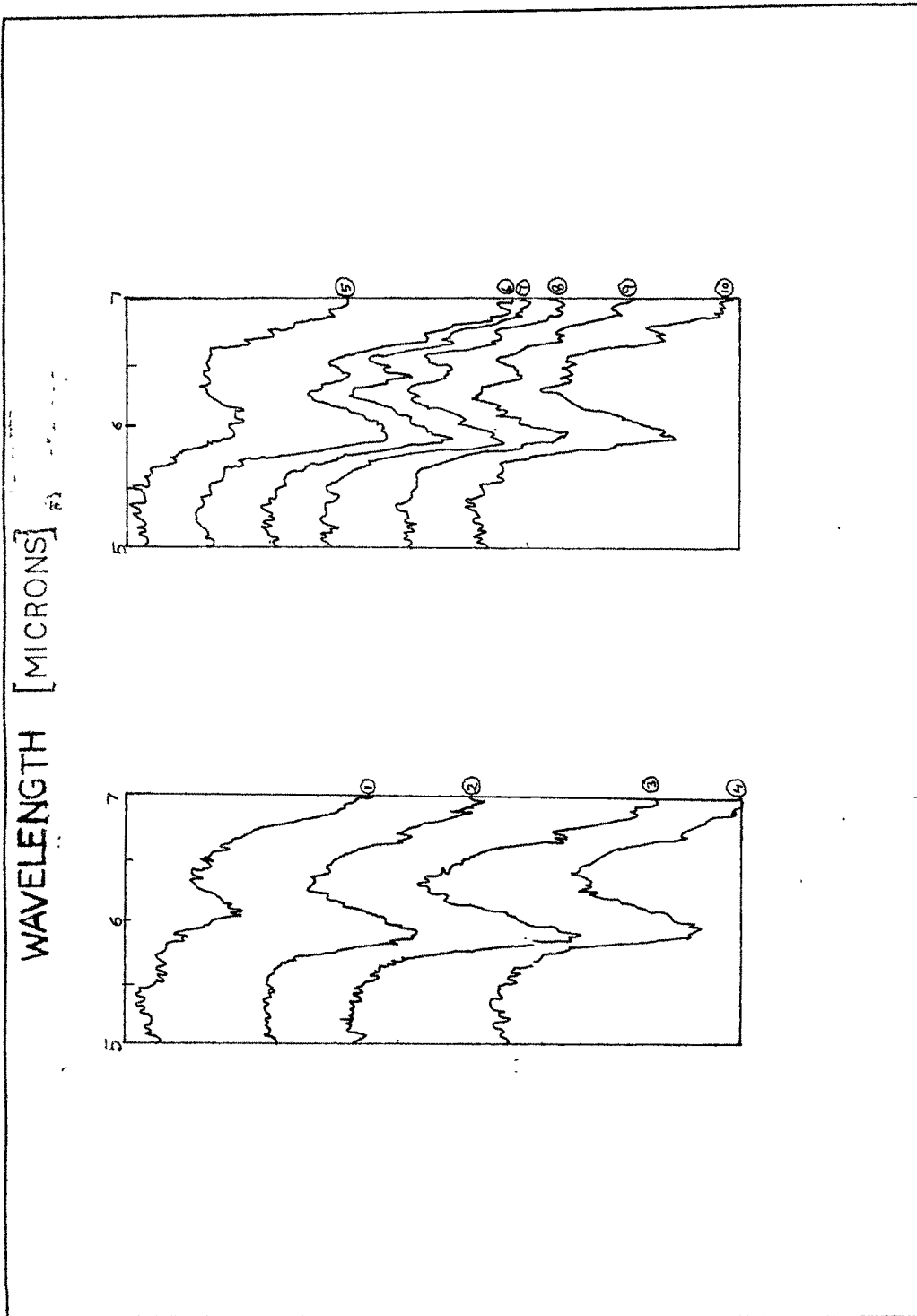
THE POSITION OF CARBONYL AND ABSORBED WATER BAND IN
THE INFRARED SPECTRA OF CELLULOSE CROSS-LINKED WITH
DMEU IN THE PRESENCE OF DIFFERENT CATALYSTS(KBr METHOD)

Spectrum No.	Treatment	Absorbed water band (μ)	Carbonyl absorption (μ)
1	Cellulose (C)	6.10 ^b	-
2	C + DMEU (D)	-	5.95 ^b
3	C + D + Zn (NO ₃) ₂	-	5.90 ^s
4	C + D + Cit. acid	-	5.90 ^s
5	C + D + Oxalic acid (pH = 4.50)	-	6.10 ^b
6	C + D + Oxalic acid (4.00)	-	5.90 ^b
7	C + D + Oxalic acid (3.50)	-	5.90 ^s
8	C + D + Oxalic acid (3.00)	-	5.90 ^s
9	C + D + Oxalic acid (2.50)	-	5.90 ^s
10	C + D + Oxalic acid (2.00)	-	5.90 ^s

s : sharp

b : broad

FIG. 36



INF RA RED SPECTRA

In short, infra red spectra of cellulose cross-linked with DMEU using organic acid catalysts show a sharp peak at 5.90 μ band. This observation is contradictory to that of Berni et al^{19,20}. This discrepancy can be explained by considering absorbed water band in cellulose. In native cellulose absorbed water band is at 6.10 μ . This absorbed water band is absent in the spectrum of the product from catalysed cross-linking reaction, as shown by Benerito et al¹⁸⁻²¹ and this can be utilized as an index of extent of cure in cross-linking operation. However, in case of the uncatalysed DMEU reaction, the water band is probably present and is superimposed on the carbonyl band resulting in a broad peak at 5.95 μ . The water band will disappear in cellulose cross-linked with DMEU in the presence of a catalyst and the net result will be the sharpening of carbonyl peak and shift to higher frequency.

The other argument generally put forward in favour of complex formation between DMEU and metal is the presence of metal in the cross-linked samples. Two sets of experiments were carried out; in the first set, samples were cross-linked with DMEU in the presence of zinc nitrate. The samples were washed with distilled water and dried. In the second set, cellulose was cross-linked with DMEU using citric acid as a catalyst. The sample was washed and dried. It was then repadded with zinc nitrate solution of a

concentration similar to that used in the first set, heated under similar conditions (120°C, 11 min, 150°C, 4 min.), washed and dried. The zinc contents of all the treated samples were determined polarographically. Table XXII shows the results.

TABLE XXII

BOUND ZINC IN THE FABRIC IN THE PRESENCE AND ABSENCE OF DMEU DURING AND AFTER CROSS-LINKING USING $Zn(NO_3)_2$ AS CATALYST

Sample	Type of treatment (% conc.)(w/v)	Zinc/100 g. of sample
1	Fabric + $Zn(NO_3)_2$ (0.25)	.0170
2	" + " (0.50)	.0198
3	" + " (1.00)	.0275
4	" + " (0.25) + (8% DMEU)	.0301
5	" + " (0.50) + (8% DMEU)	.0556
6	" + " (1.00) + (8% DMEU)	.0772
7	" + 0.25 Cit. acid + (8% DMEU)	Nil
7	Repadded with 0.25 $Zn(NO_3)_2$.0268
7	" " 0.50 "	.0498
7	" " 1.00 "	.0674

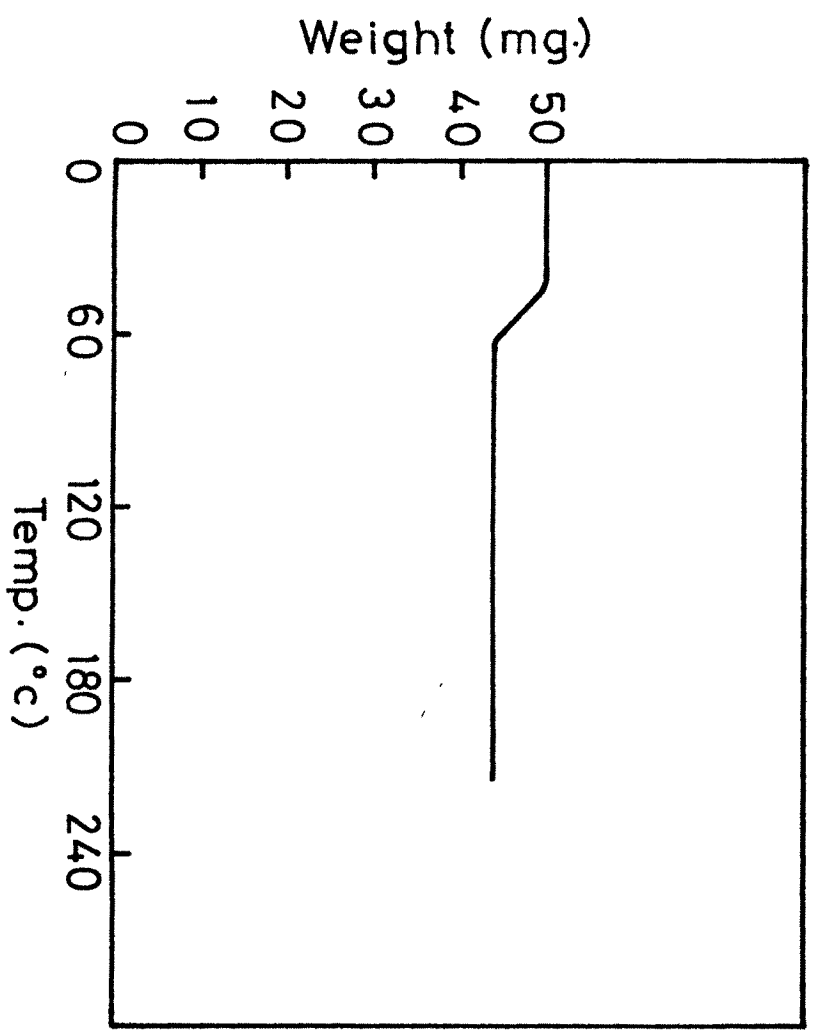
The experiments on estimation of bound zinc on the fabric in the presence and absence of DMEU during and after cross-linking show that the quantity of the zinc fixed on the fabric in the

absence of DMEU is less than in the presence of DMEU. The quantity of bound zinc increases with the concentration of zinc in the pad bath. In the case of cellulose cross-linked with DMEU, the quantity of bound zinc present in the two cases, i.e. (i) when zinc nitrate is present during cross-linking (ii) zinc nitrate is padded after cross-linking, was almost the same. This indicates that the presence of zinc in the cross-linked cellulose may or may not be due to complex formation between resin molecule and polyvalent metal. Even if complex formation occurs, it may not be the factor solely responsible for the catalytic activity of the metal salt for the cross-linking.

In recent years various research groups have reported highly active catalysts for the cross-linking of cellulose with formaldehyde or amido-formaldehyde adducts¹⁻⁴. The highly active catalysts are formed from the combination of certain metal salts and organic acids or from the combination of metal salts with partially or completely neutralized organic acid metal salts. The mechanism of the high catalytic activity of such catalyst has not been explained fully uptill now. In the present work some data on the thermal behaviour of such catalysts are presented.

Succinic acid and sodium chloride were subjected to thermogravimetric analysis (TGA) in an air atmosphere. Fig. (37) shows

Fig. 37 Weight Losses on Heating
Sodium Chloride



the result of these experiments. When sodium chloride alone is treated, it loses 5 - 6 mg. weight between temperature 45° - 60°C. Above 60°C no weight loss is observed upto 210°C. When the heating is completed, a white residue remains. In case of succinic acid alone no weight loss is observed upto 160° - 164°C. From 160° - 164°C onwards succinic acid starts losing weight which continues upto 210°C. The total weight loss is 22 - 24 mg. The residue left over is white. When a mixture of sodium chloride (50 mg) and succinic acid (50 mg) is heated, weight loss starts at 45° - 47°C and at 60°C, it amounts to 5 - 6 mg. In the temperature range 60°C to 148°C, there is no further weight loss. However, the mixture starts losing weight again at 148° - 150°C and a weight loss of 35 - 37 mg. is observed in the range 150° - 210°C. The mixture of sodium chloride and succinic acid shows characteristic weight loss of sodium chloride at 45° - 60°C. However, the second weight loss starts at a lower temperature and is 10 - 12 mg. more than in case of succinic acid alone. The residue left in the case of mixture is brown in colour. This additional weight loss may be due to decarboxylation of succinic acid, accelerated due to the presence of metal salts or to following displacement reaction.

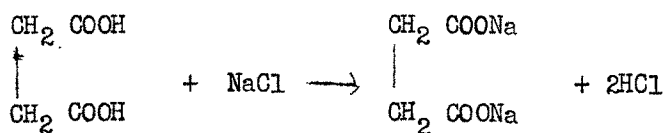
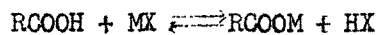


Table XXIII gives the data of strength losses of a cotton poplin heated in presence of different catalysts. The mixture of organic acid with the metal salt causes significantly more loss in tensile strength than the metal salt or acid alone. Inorganic and organic acids hydrolyze cellulose, the extent of hydrolysis depending on the dissociation constant of the acid. Latent acid type metal salts also liberate acid at high temperatures and thus hydrolyze cellulose, resulting in a loss in tensile strength. Therefore, the increased losses in case of mixed catalysts can be attributed to the formation of a larger quantity of inorganic acid, because the displacement reaction between the metal salt and the organic acid (RCOOH), shown below, can liberate the acid.



M = metal cation

X = anion

When a solution containing an organic acid with magnesium chloride is heated, it is observed that HCl gas is liberated. For a quantitative study, the distillate was collected and titrated against 0.1N sodium hydroxide. The results of titration are given in Table XXIV.

TABLE XXIII

EFFECT OF HEATING ON TENSILE STRENGTH OF COTTON
POPLIN CLOTH IN PRESENCE OF DIFFERENT CATALYSTS

Catalyst	%(owf)*	Tensile strength(Kgs)		
		Dry 120°C/ 1 min.	Dry 120°C/ + 1 min.	Cure 150°C/ 4 min.
ZnCl ₂	0.60	37.8		32.4
Zn(NO ₃) ₂	0.37	37.5		37.7
Cit. acid	0.187	37.9		38.0
ZnCl ₂ + Cit. acid	0.60 + 0.187	37.0		22.1
Zn(NO ₃) ₂ + Cit. acid	0.37 + 0.187	29.3		13.4
Untreated		40.8		

* (owf = on weight of fabric)

TABLE XXIV

AMOUNTS OF HCl LIBERATED ON HEATING MIXTURES OF
ORGANIC ACIDS AND METAL SALTS

Acid	pK ₁	ml. of 0.1N NaOH consumed by liberated acid.	
		NaCl	MgCl ₂
Oxalic acid	1.19	28.2	125.0
Tartaric acid	3.02	15.0	84.0
Citric acid	3.06	9.2	76.0
Malic acid	3.40	7.0	50.0
Succinic acid	4.19	3.4	25.0

In each experiment significant quantity of acid is liberated. The amount of acid liberated is inversely proportional to the pK₁ value of the organic acid used.

Higher volatility of halogen acids compared to that of the organic acids is responsible for their displacement from the metal halides, because it is well known that an acid can be displaced from its salt by another acid of higher boiling point. Even relatively weak acids, like boric and silicic acids, displace much stronger acids from their salts owing to the lower volatility of the weak acid. Ephram²² has reported that halogen acids are formed

when solutions containing halogen ions and hydrogen ions are mixed. Various methods of generating hydrochloric acid such as Mond's method²³ ($\text{NH}_4\text{Cl} + \text{H}_2\text{SO}_4$), Witt's method²³ ($\text{NH}_4\text{Cl} + \text{H}_3\text{PO}_4$) and Grineva's method²⁴ are based on this reaction. On the basis of explanation given above the probable reason for higher weight losses in case of the mixture of sodium chloride with succinic acid is the formation of hydrochloric acid and its volatilization.

TABLE XXV

EFFECT OF THE PRESENCE OF NaCl AND OXALIC ACID ON
THE PROPERTIES OF COTTON POPLIN TREATED WITH DMEU(6% owf)*

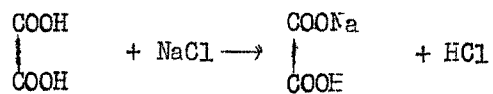
Dried at 120°C/1 min.
Cured at 150°C/4 min.

Oxalic acid added added %(owf)*	NaCl added %(owf)*	pH of pad bath	Crease recovery angle(W+F)				Tensile st.(kg)	
			On drying		On curing		On drying	On curing
			WCR	DCR	WCR	DCR		
0.15	-	2.50	244	225	255	267	29.3	23.7
0.15	0.37	2.50	254	260	260	279	25.6	21.3
-	0.37	7.10	158	154	160	154	42.0	
Untreated	-	-	160	154			42.0	

* owf = on weight of fabric

Table XXV shows some results of the treatment of cotton fabric with dimethylol ethylene urea. Sodium chloride does not catalyse

the reaction of DMEU with cellulose but in the presence of oxalic acid it increases the catalytic activity of the acid, as seen from the results of wet and dry crease recovery. The displacement reaction shown below is favoured by the increased volatility of hydrochloric acid.



These experiments again confirm earlier observations.

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