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Dyeing of cotton with sulphur dyes using alkaline catalase as reduction catalyst

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Attempts have been made to dye cotton with alkaline catalase to observe if sodium sulphide can be replaced with it. It is observed that the alkaline catalase is too capable of developing comparable dyebath potential, dye receptivity on cotton, reduction bath stability as well as colourfastness of dyeings as obtained in sodium sulphide based reducing systems.

Keywords: Cotton, Catalase, Dye receptivity, Sulphur dye, Sodium sulphide

1 Introduction

Sulphur dyes are complex organic compounds, inconsistent in composition and are synthesized by heating simple amines or phenolic compounds in presence of sulphur. Because of water insolubility, these dyes are reduced and solubilised with sodium sulphide to respective sodium salts, thus possessing affinity for cellulose. The advantages associated with the use of sulphur dyes are their cheapness and excellent colourfastness except against chlorine[1-9]; only deep shades such as black, navy blue, green, khaki are developed. Sodium sulphide applied for reduction and solubilisation is highly toxic in nature, produces hydrogen sulphide, corrodes concrete supply pipes and increases sulphur content in waste water[2,10].

Alternate eco-friendly reducing agents, viz. glucose-NaOH, reducing sugar, electrochemical reduction, hydroxyacetone, etc were not found comparable to sodium sulphide due to inherent limitations[11-13]. Certain specific enzymes are found reducing in nature, and may catalyze reduction of dyes[14,15]. Catalase (EC 1.11.1.6) belonging to oxido reductase class is used in textile bleaching, electronics, sterilization of liquid food products and conversion of residual hydrogen peroxide to oxygen and water. The industrial application of catalase is wide-ranging because of its substrate (H_2O_2), which is frequently used as a strong biocide, oxidant and bleaching agent in the textile, pulp and paper, wood and food industries[16,17]. Immobilized thermo-alkali-stable bacterial catalase-peroxidases are recommended for the treatment and recycling of the textile bleaching effluents to be reused for dyeing[18-20].

Catalase is applied for organic phase biosensing by immobilizing the enzyme onto a glassy carbon amperometric transducer by casting a mixed enzyme[21]. The O_2-scanvanging effect of the GOX/CAT systems has potential food related applications, viz. in the control of lipid peroxidation, and enzymatic and non-enzymatic browing[22-24]. H_2O_2-consuming enzymes like catalase is deleterious for aerobic micro organisms because of the fast depletion of available oxygen and hence can be used as antimicrobial agents[25,26]. Catalase is redox active manganese-containing enzymes and contains two manganese ions at its active sites. It influences protection of an organism from the potential deleterious effects of the reduced forms of dioxygen and hydrogen peroxide[15,26-28]. Catalase enzymes complete their catalytic cycle in 2-2 electron reduction and oxidation. An attractive alternative to neutralize the residual bleach chemical is catalase enzyme. It does not require any rinsing and acts in cold water, thus saving energy and water. The reaction rate is very fast and it acts in alkaline range.

In this work, pretreated cotton is dyed with sulphur dyes using sodium sulphide and alkaline catalase separately at boil. Performance of two reduction systems are compared in terms of reduction potential of dyebath at various stages of dyeing, dye receptivity of dyed cotton, stability of bath as well as fastness properties of dyeings.

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2. Materials and Methods

2.1 Materials

Pretreated and mercerized cotton fabric (ends/dm 362, picks/dm 284, warp 20^s, weft 30^s and gsm 156) was used in this study.

2.2 Chemicals

Catalase and ten different sulphur dyes were procured from Clarient and Sulfast, Mumbai, India, respectively whereas sodium sulphide (LR, 55-60%), sodium chloride (AR, 99.5%), sodium hydroxide (AR, 96%), acetic acid (AR, 99.8%) and potassium dichromate (AR, 99.8%) were procured from S D Fine Chemicals.

2.3 Equipment

Computer color match (Datacolor Check, Datacolor International, US), light fastness tester (Paresh Engineering Works, Ahmedabad, India), wash fastness tester (RBC Electronics, Mumbai, India) and crockmeter (Paramount, Delhi, India) were used to evaluate dye receptivity (*K*/*S*), colorfastness through AATCC test methods 16-2004 (light), 61-2007 (wash), 8-2007 (rubbing) respectively. Digital *p*H cum ORP meter (Century Instruments, Chandigarh, India) was used to assess dyebath *p*H and redox potential using reference electrode Ag/AgCl and the combined electrode Pt-Ag/AgCl filled in with saturated KCl solution to measure ORP.

2.4 Dyeing of Cotton with Sulphur Dyes

Dyebath was prepared with sulphur dye (5%) and sodium sulphide (0.5-5 times, based on weight of dye) at a liquor ratio of 20. The bath was heated at 90-95°C and stirred well until dye was completely reduced and solubilised. Cotton fabric was dyed in this bath for 30 min followed by addition of salt (sodium chloride, 20 g/L) and further dyeing for 90 min at this temperature. Dyed cotton was cold washed, oxidized with acetic acid and potassium dichromate (1g/L each) at 50-60°C for 30 min followed by soaping at boil and final wash. In catalase system, preparation of dyebath, dyeing of cotton and oxidation of dyeing were carried out similarly as in sulphide system. However, sodium sulphide was replaced with catalase (0.05-1.5 times of dye) alongwith sodium hydroxide for corresponding dyebath pH.

2.5 Stability of Reduction Baths

To study reduction bath stability in absence of dye, reduction baths in both sulphide and alkaline catalase systems were prepared and stored for a specific period (0-24 h) at 90-95°C, after which the *p*H and reduction potential were noted down. Dye was added and after reduction and solubilisation, cotton was dyed in these baths. To study reduction bath stability in presence of dye, dye baths were prepared and stored for a specific duration at 90-95°C, after which the *p*H and reduction potential were noted down and cotton was dyed in these baths.

2.6 Evaluation of Dyebath and Dyed Samples

Cotton fabric dyed separately in sulphide and alkaline catalase based dyebaths were evaluated for dye receptivity (*K*/*S*) and colour fastness properties while reduction baths were evaluated for the reduction potential as well as *p*H at various stages of dyeing, i.e. before and after reduction of dye as well as at the end of dyeing.

3 Results and Discussion

3.1 Dyeing of Cotton using Sodium Sulphide

Cotton was dyed with ten different sulphur dyes using sodium sulphide as reducing agent at various concentrations followed by oxidation with potassium dichromate and acetic acid. The dye receptivity of the samples was evaluated (Table 1).

3.2 Dyeing of Cotton using Alkaline Catalase

To explore the capability of catalase to reduce sulphur dyes, dyebaths were prepared with five different sulphur dyes, viz. Black 1, Blue 1, Green 1, Red 2 and Yellow 2. The *p*H values of all these baths were maintained at around 12 using NaOH, as it was developed in sulphide based dyebaths, followed by addition of catalase at a concentration equivalent to that of dye (1T). The temperature of all the baths was raised to 90-95°C and dyeing was carried out in the same way as was followed in sulphide system. The dyebath status and dye receptivity of cotton are shown in Table 2.

Experimental results show comparable efficiency of catalase based dyebaths with those obtained in sulphide system. Reduction potential in all the three stages of dyeing indicates complete reduction of dye, which ranges from -500 mV to -550 mV. The dye receptivity results confirm reduction and solubilisation of dye with catalase. Although the results do not show complete match with those obtained in sulphide system, it was realized that the optimization of dyeing parameters may improve the results.

Table 1—Influence of sodium sulphide (2T)* on dyebath status and dye receptivity

Sulphur dye (λ_{max}, nm)	Reduction potential (mV) and *p*H at various stages						Dye receptivity
	Before dye reduction		After dye reduction		At the end of dyeing		
	*p*H	mV	*p*H	mV	*p*H	mV	
Black 1 (590)	11.4	-555	11.2	-520	10.9	-504	18.1
Blue 1 (580)	11.4	-560	11.2	-530	11.0	-508	6.2
Green 1 (460)	11.4	-556	11.0	-535	11.0	-518	7.9
Red 2 (510)	11.2	-558	11.1	-531	10.9	-524	9.0
Yellow 2 (400)	11.5	-543	11.2	-530	11.1	-511	3.8
Blue 5 (600)	11.5	-538	11.3	-534	11.2	-523	5.9
Green 18 (400)	11.4	-562	11.2	-538	11.0	-517	6.7
Green 8 (400)	11.5	-532	11.1	-507	11.3	-525	3.1
Brown 14 (400)	11.4	-560	11.3	-535	11.2	-513	10.8
Green 21 (400)	11.6	-538	11.4	-518	11.2	-510	7.9

* Double amount (2T, g) to weight of dye (T, g).

Table 2—Dye bath status and dye receptivity in catalase system

Dye	Reduction potential (mV) and *p*H at various stages						Dye receptivity
	Before reduction of dye		After reduction of dye		At the end of dyeing		
	*p*H	mV	*p*H	mV	*p*H	mV	
Black 1	2.0	-567	11.8	541	11.7	-528	18.6
Blue 1	12.0	-568	11.7	-539	1.5	-517	6.3
Green 1	12.0	-562	11.8	-535	11.7	-518	7.9
Red 2	2.0	-558	11.8	-549	11.7	-511	10.1
Yellow 2	12.0	566	1.5	-540	11.5	-513	7.4

3.2.1 Influence of Dyeing Parameters

Early studies and experiments suggested the capability of catalase to reduce and solubilize sulphur dyes in alkaline conditions. Reduction potential of dyebaths in all three stages shows complete reduction of dye which ranges from -500 mV to -550 mV. The dye receptivity (*K*/*S*) results of various dyes also confirm reduction and dyeing of sulphur dyes using catalase. Dyeing parameters viz. concentration of catalase and electrolyte, *p*H, temperature and time of dyeing have been optimized to improve the results and to formulate a standard workable recipe. Five sulphur dyes of different hues, viz. Black 1, Blue 1, Green 1, Red 2 and Yellow 2 were selected for optimization and study of dyebath status as well as dye receptivity. Dyeing variables initially considered were those followed in sulphide based dyeing process, i.e. salt (20 g/L), temperature (90-95°C), and time (2 h) except catalase concentration (1 T, i.e. equal to the weight of dye). Gradual increase in the amount of sodium hydroxide increases the reduction potential and pH of bath in the same rate; even the dye receptivity values follow the same pattern [Fig. 1(a)]. The maximum reduction potential and

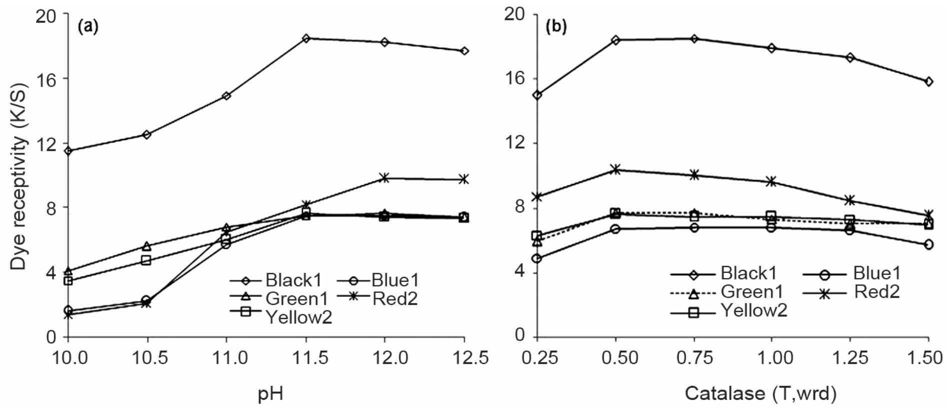

Fig. 1—Effect of (a) *p*H and (b) catalase concentration on dye receptivity

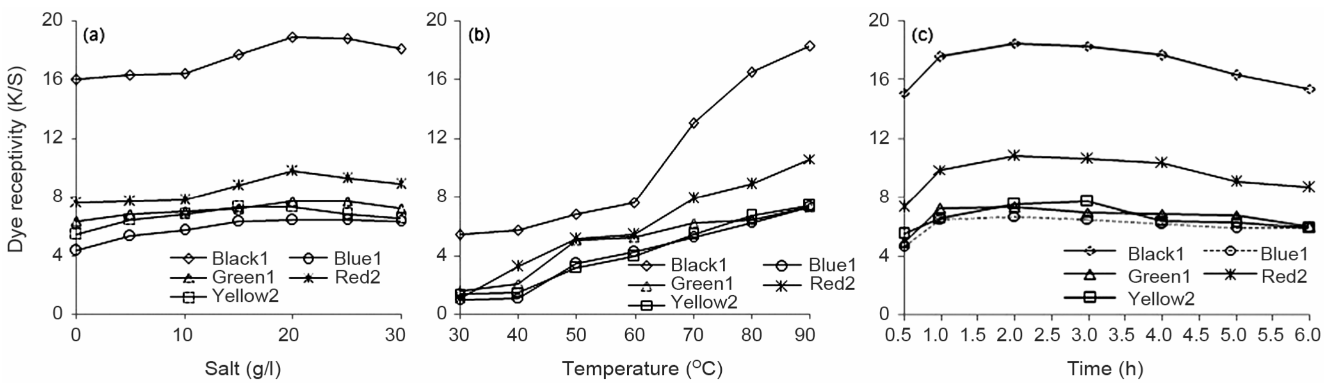

Fig. 2—Influence of (a) salt, (b) temperature, and (c) time on dye receptivity

dye receptivity are achieved at 12 *p*H. Effect of catalase concentration was further studied (0.25-1.5T, T: weight of catalase in times weight of dye), keeping the dyebath at *p*H 12 and other parameters as stated earlier. It is observed that the catalase concentration of 0.5T is adequate to cause effective reduction of dye supported by maximum reduction potential at this catalase concentration. The dye receptivity data are reported in Fig. 1(b). In further study, *p*H was maintained at 12 and catalase concentration at 0.5T; salt concentration was varied to observe increase in exhaustion, which was also invariably followed in sulphide based dyeing process. Addition of common salt (NaCl) at various concentrations (0-30 g/L) could not cause any substantial increase in dye receptivity. Marginal increase in dye receptivity is noted at 15-20 g/L salt and no such increase is found beyond that level [Fig. 2(a)]. However, the increase in dye receptivity in case of Black 1 and Red 2 dyes might be attributed to their lower molecular weights as well as zeta potential. This results in higher dye receptivity for these two dyes even at lower salt concentration because of more physical forces of attraction between these two dyes and cotton but the increase was not substantial with other dyes. Dyeing at various temperatures shows progressive increase in reduction potential and dye receptivity of cotton proportionately. Maximum dye receptivity on cotton is noticed at 90°C [Fig. 2(b)]. Increase in dyeing time beyond 2 h shows reduction in dye receptivity of cotton [Fig. 2(c)]. The optimum parameters for dyeing cotton with sulphur dyes using alkaline catalase could be summarized as *p*H 12, catalase concentration 0.5T (wrd), salt (nil), temperature (90°C) and a dyeing time 2 h. Finally, cotton was dyed with ten different sulphur dyes using these optimum parameters and the dye receptivity values thus obtained for each dye was compared with those obtained in sulphide system (Fig.3). Black 1, Green 1, Green 21 and Brown 14 show comparable dye receptivity in both the systems; Blue 1, Blue 5, Green 18 and Green 8 show little less dye receptivity while Red 2 and Yellow 2 show higher dye receptivity in catalase system.

3.3 Stability of Reduction Bath

3.3.1 In Absence of Dye

The stability of reduction baths prepared separately with sulphide and alkaline catalase was studied in absence of dye. For this purpose, reduction baths were prepared in both the systems and stored for a specific time at 90°C. The changes in *p*H and reduction potential were noted down after storing for specific time and thereafter dye (Yellow 2, 1%) was added in each bath. Cotton fabric was dyed in these baths for 2 h as done in sulphide and catalase systems and dye receptivity was assessed. Both sulphide and catalase based reduction baths retain their reducing capability till 24 h of storage, in general, in absence of dye in terms of reduction potential and *p*H both (Table 3).

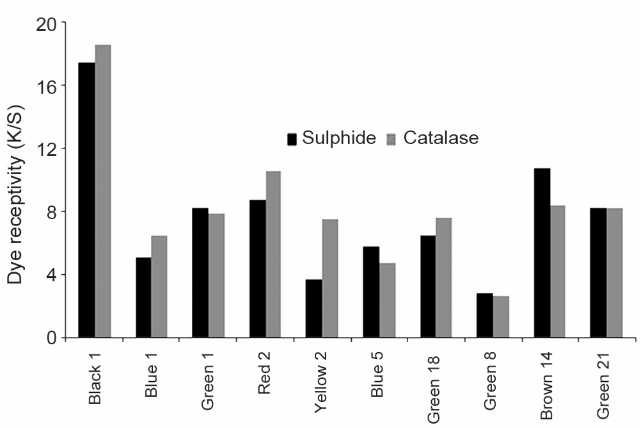

Fig. 3—Comparison of dye receptivity (*K/S*) in sulphide and catalase systems

In sulphide based baths, there is increase in reduction potential upto 2 h of storage but thereafter it shows gradual fall. The potential values of baths remain quite effective for reduction of dye upto a storage time of 6 h though the reduced status could not be maintained till end of dyeing. Only the bath stored for 2 h shows effectiveness to completely reduce dye and retain the reduced status till end of dyeing, as marked by dye receptivity values [Fig. 4(a)]. Catalase based baths also show stability upto 2 h and then shows gradual fall till 24 h though *p*H remains as high as 12 for all the storage times. The effectiveness of stored baths towards reduction of dye and the maintenance of reduced form till end of dyeing remain as such just after 2 h of storage (Table 3).

The dye receptivity of cotton dyed from all these stored baths could be seen in Fig. 4(a). A gradual increase in dye receptivity of cotton from both the sulphide and catalase based dye baths is observed for first 2 h followed by gradual fall. Dye receptivity remains maximum after storage for 1h in catalase based bath and thereafter starts decreasing.

3.3.2 In Presence of Dye

In practice, fresh dyebaths meant for dyeing are not used immediately in some cases and sometimes lapse occurs due to various reasons; even exhausted dye baths are sometimes not drained out rather fortified for spent chemicals and dye for reuse of bath. To study potential of stored dye baths towards successful dyeing, reduction baths were prepared in sulphide and catalase systems followed by addition of dye (Yellow 2, 1%) and stored for 24 h. The dye baths in sulphide system show required reduction

Table 3—Stability of reduction baths in absence of dye

Time h	Reduction potential (mV) and *p*H at various stages											
	Before dye reduction				After dye reduction				At the end of dyeing			
	*p*H		mV		*p*H		mV		*p*H		mV	
	Sul	Cat	Sul	Cat	Sul	Cat	Sul	Cat	Sul	Cat	Sul	Cat
0	12.0	11.8	-501	-523	11.6	11.8	-409	-517	11.2	11.7	-400	-507
1	12.0	11.8	-544	-538	11.7	11.7	-509	-519	11.2	11.6	-440	-514
2	12.0	11.6	-560	-534	11.6	11.4	-536	-519	11.2	11.2	-525	-510
4	12.0	11.5	-542	-528	11.5	11.3	-510	-519	11.3	11.2	-418	-502
6	12.0	11.4	-509	-519	11.6	11.2	-478	-506	11.4	11.2	-413	-486
8	11.9	11.2	-481	-512	11.5	11.1	-430	-493	11.4	11.0	-400	-478
24	11.9	10.8	-454	-453	11.1	10.7	-415	-452	11.0	10.6	-312	-444

Sul—Sulphide, Cat—Catalases.

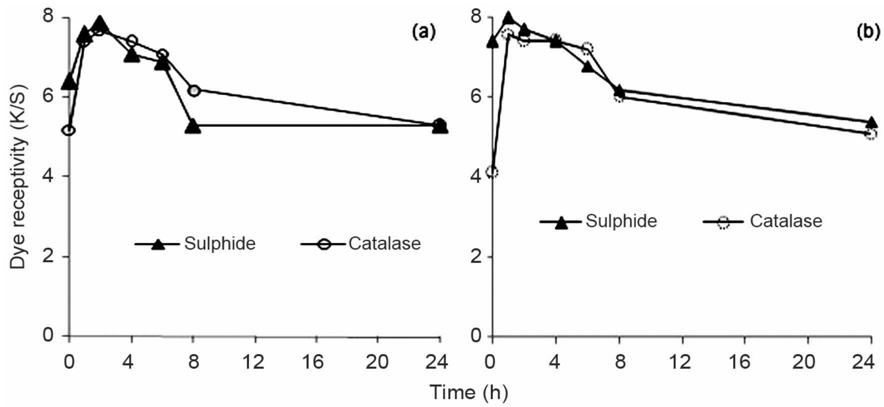

Fig. 4—Stability of dye bath in (a) absence and (b) presence of dye

Table 4—Stability of dyebaths in presence of Yellow 2

Time h	Reduction potential (mV) and *p*H at various stages								Dye receptivity	
	Before dyeing				After dyeing				Sul	Cat
	*p*H		mV		*p*H		mV			
	Sul	Cat	Sul	Cat	Sul	Cat	Sul	Cat		
0	12.0	11.7	-528	-510	10.8	11.6	-502	-481	7.4	4.1
1	12.0	11.7	-532	-522	10.8	11.6	-508	-521	8.2	7.6
2	12.0	11.6	-546	-521	11.7	11.5	-500	-514	7.7	7.4
4	12.0	11.4	-508	-516	10.7	11.3	-418	-510	7.4	7.4
6	11.9	11.3	-501	-512	10.6	11.2	-391	-502	6.8	7.2
8	11.8	11.2	-482	-478	10.3	11.1	-338	-453	6.2	6.0
24	11.6	10.8	-461	-404	9.6	10.6	-347	-378	5.4	5.1

potential throughout dyeing upto a storage time of 1 h, beyond which though the starting reduction potential remains adequate enough, the end potential (potential after dyeing) starts decreasing progressively (Table 4), indicating inadequate reduction of baths towards the end of dyeing.

Catalase based reduction baths show similar stability. The baths show good potential upto a storage time of 8 h, but the effectiveness of bath is only for a storage time of 1 h throughout dyeing (Table 4). Baths stored beyond 1 h show substantial fall in reduction potential at the end of dyeing due to which dyeing is stopped before completion of 2 h of dyeing time. The comparative dye receptivity of cotton obtained from both these reducing systems is shown in Fig. 4(b).

3.4 Fastness Performance

Wash, light and rub fastnesses of cotton dyed in sulphide and catalase systems were evaluated and compared. The results are shown in Table 5.

The light fastness of dyed cotton remains very good to excellent and almost same in both the systems for all ten dyes under study. Wash fastness shows the same pattern, i.e. very good to excellent (4-5) in both the reducing systems. Dry rubbing shows almost same and very good to excellent fastness for all dyes under study while in wet rubbing, results are comparable to those from dry rubbing except for Yellow 2 which results in moderate to good wet rubbing fastness. In general, all four types of colour fastness of cotton dyed in catalase system show good comparative performance with those dyed in sulphide system.

4 Conclusion

The studies on alkaline catalase and sodium sulphide for dyeing of cotton with sulphur dyes at boil show comparative dye receptivity of cotton with little variation. Stability of reduced baths in absence and presence of dye shows good stability for 24 h, though the bath stability is found better in presence of dye.

Table 5—Fastness of dyed cotton

Dye	Wash fastness		Rub fastness		Light fastness
	Fading	Staining	Dry	Wet	
Black 1					
Sulphide	5	5	5	4	6
Catalase	4-5	4-5	5	4-5	6
Blue 1					
Sulphide	4	4	5	4-5	5
Catalase	4	4	4	4-5	5
Green 1					
Sulphide	4	4	5	4-5	6
Catalase	4-5	4-5	4-5	4-5	6
Red 2					
Sulphide	4	4	5	5	6
Catalase	4	4	4	4	6
Yellow 2					
Sulphide	4	4	4	3-4	5
Catalase	4-5	4-5	5	4	5
Blue 5					
Sulphide	4-5	4-5	5	5	4
Catalase	4	4	5	4	4
Green 18					
Sulphide	4-5	4-5	5	4-5	6
Catalase	5	5	5	4-5	6
Green 8					
Sulphide	4-5	5	5	4-5	6
Catalase	4-5	4-5	5	4-5	6
Brown 14					
Sulphide	4-5	4-5	4-5	4-5	6
Catalase	4	4	5	4-5	6
Green 21					
Sulphide	4-5	4-5	4-5	4	5
Catalase	4-5	4-5	4-5	4-5	5

Colourfastness of dyed cotton is found to be very good to excellent for all dyes, except Yellow 2 where wet rubbing is moderate to very good for both the systems.

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