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A New Method for the Determination of the Bleach Index of Lac

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The bleaching characteristic of any sample of lac is generally expressed in terms of its bleach index or bleachability. In the different methods currently in use for determining the bleach index or bleachability of lac, the lac samples are treated with the required amount of bleach liquor so as to result in " complete " bleaching and the volume of bleach used up is noted. In the new method described, the same amount of bleach liquor is added to all samples of lac and the degree of bleaching effected in each case is determined from the colour of the bleached solution (filtered free from wax) in terms of N/1,000 iodine.

The advantages of the new method over the existing ones are: (1) no standard seedlac is required, (2) repeated additions of small quantities of bleach liquor (from time to time) and repeated filtrations and testings are avoided, and (3) the necessity of different procedural details for different grades of lac is eliminated. The comparison of the colour of the bleached lac solutions is simple, quick and accurate, and the results obtained are independent of moderate variations in laboratory temperature.

BLEACHED lac is one of the major forms in which lac resin is put into practical use. Large quantities of bleached lac, both regular and refined, are annually manufactured in foreign countries, especially in the United States, United Kingdom and Germany. America alone is estimated to be manufacturing over 7,000 tons of bleached lac annually. The chief raw materials used are shellac and seedlac. The latter is finding increasing favour as this material is invariably free from orpiment and rosin which are sometimes mixed in certain grades of shellac for better appearance and flow and which are very detrimental for bleaching purposes.

Crude lac, in its natural form, contains two colouring matters. One of them is a water-soluble dye known as laccaic acid[1] and the other a water-insoluble but spirit-soluble dye called erythrolaccin[2]. When crude lac is refined into seedlac by crushing and washing with water, with or without the addition of mild alkaline reagents such as sodium carbonate or triethanolamine, practically the whole of the water-soluble laccaic acid is removed. Seedlac and shellac are, therefore, practically free from this dye. The material that imparts to shellac and seedlac the familiar pale yellow to deep reddish brown colour is erythrolaccin. The methods used in the bleaching of lac aim at eliminating or destroying erythrolaccin. This dye can be removed by physical methods such as treatment with decolourizing agents or it can be transformed into colourless derivatives by reduction or oxidation. Reductive processes lighten the colour of shellac solution which, however, darkens on exposure to air due to reversion of the quinol to quinone system in the dye[3-4]. Oxidative bleaching of lac includes both chemical[5-16] and electrolytic[17-18] methods. The most widely used bleaching agent in commercial practice is sodium hypochlorite.

The bleaching characteristics of different specimens of seedlac and shellac differ widely depending upon a number of factors and are of considerable importance in grading lacs for purposes of bleaching. There is apparently no definite relation between the depth of colour of lac and its bleachability.

Bleaching characteristics of lac are expressed in terms of " bleach index " or the recently introduced term " bleachability ". " Bleach index " is usually determined by treatment of an alkaline solution of lac with sodium hypochlorite (3 per cent available chlorine) under definite conditions. The number of cubic centimeters of sodium hypochlorite required to bleach a solution of the lac to the desired end-colour is the bleach index. Bleachability is assessed by adding specific amounts of standard sodium hypochlorite to the alkaline lac solution and by comparing the end-colour with that of standard samples of seedlac bleached under the same experimental conditions. Bleachability is categorized into four groups requiring 80, 100, 115 and 140 cc. respectively of bleach liquor for 30 g. of the lac to produce a shade equal to, or lighter than, the shade produced by standard samples under identical experimental conditions[19].

The bleach index methods[20] used or advocated, although basically similar, differ in procedural details, particularly in regard to (1) particle size of the test sample, (2) method of dissolution of lac, and (3) determination of end-colour.

Particle size — The degree of fineness of seedlac samples influences the consumption of bleach liquor[21,22]. Finely ground samples enhance the solubility of nitrogenous matters present in seedlac and thereby increase the demand for bleach. Fineness of samples currently recommended for bleach index or bleachability determination is recorded in Tables 1 and 2.

The need for a uniform particle size of the samples is obvious from the data presented in Tables 1 and 2. As a result of a series of experiments carried out by us it was found that samples ground to pass through a 10-mesh sieve gave uniformly satisfactory and reproducible results. No advantage appears to be gained by grinding the sample finer. This particle size has the additional advantage of being more in line with the actual works practice as seedlacs are not generally powdered fine for use in the manufacture of bleached lac.

Extraction — All the existing methods specify approximately 10 per cent anhydrous sodium carbonate on the weight of seedlac taken. But in respect of other details, there is some divergence of opinion. These are brought out in Table 3.

Seedlac samples were extracted under all the conditions detailed in Table 3. It was found that when the extraction was carried out at 65°±2°C., the voluminous froth accumulating over the surface of the extract did not subside within 1 hr. Further, most of the wax was left over as residue during subsequent filtration. When the extraction was carried out at the temperature of boiling water and with mechanical stirring, the frothing in the initial stages was so uncontrollable that the solution often overflowed the sides of the beaker vitiating the experiment. Hand-stirring while extracting at the temperature of boiling water was found to be quite convenient and dissolution was complete within half an hour. Extraction for a longer period (say, 1 hr.) is, therefore, unnecessary and only leads to further darkening of the extract.

TABLE 1 — PARTICLE SIZE OF SEEDLAC FOR BLEACH INDEX DETERMINATION

Method	Particle size of sample	
	Kusmi	Baisakhi
Angelo Bros., Calcutta	To be used as such if free; to be ground to pass through 10 mesh sieve, if blocked	To be used as such if free; to be ground to pass through 10 mesh sieve, if blocked
Indian Lac Research Institute (ILRI)	do	do
United States Shellac Importers' Association (USSIA)	40 mesh	40 mesh

TABLE 2 — PARTICLE SIZE OF SEEDLAC FOR BLEACHABILITY TESTS

Method	Particle size of sample	
	Grade I A and B mesh	Grade II A and B mesh
USSIA	40	40
Indian Standards Institution (ISI)	40	10

TABLE 3 — DISSOLUTION OF SEEDLAC

Method	Temp.	Mode of stirring	Duration hr.
Angelo Bros., Calcutta	65°±2°C.	Mechanical	1
ILRI	Boiling water	Manual	1
USSIA (bleach index)	do	do	1
USSIA (bleachability)	do	Mechanical	1
ISI	do	do	½

Preparation of bleach liquor — The usual methods recommended are: (1) treating a suspension of good quality bleaching powder with sodium carbonate solution and filtering off the precipitated calcium carbonate, and (2) direct chlorination of sodium hydroxide or carbonate. Since it is not always easy to obtain bleaching powder of the required quality, method (1) is not always convenient. Again, a stable bleach liquor of 3 per cent available chlorine is difficult to obtain starting from sodium carbonate. Preparation of bleach liquor by chlorination of sodium hydroxide is free from these limitations and a bleach liquor of approximately 5 per cent available chlorine can be conveniently prepared by passing chlorine gas through ice-cooled 1·5N solution of caustic soda. The associated sodium carbonate that is invariably present in caustic soda has no deleterious effect on the stability or efficiency of the bleach liquor.

Free alkalinity of bleach liquor — The stability of a hypochlorite solution is directly proportional to its free alkalinity while its bleaching efficiency is just the reverse. For the bleaching of lac what is required is a bleach liquor of reasonable stability and high bleaching efficiency. This means that the bleach liquor should contain only the minimum amount of free alkali. As a result of a series of experiments carried out by us it has been found that a sodium hypochlorite solution with a free alkalinity of 0·02-0·04N serves quite well for the purpose. A higher amount of free alkali increases the bleach consumption and reduces the bleaching rate while with lower amounts the liquor is rather unstable. A bleach liquor containing this range of free alkali may be conveniently made by controlling the degree of chlorination by the following simple test. Approximately 1 cc. of the solution is transferred periodically to a test-tube and treated with one drop of 0·5 per cent phenolphthalein solution. Chlorination is continued up to the point when a distinct pink colouration is noticed and which persists for not more than 5 sec. Several batches of sodium hypochlorite solution were prepared according to this procedure and all of them were found to have free alkalinities within the range of 0·02-0·04N. These were found to be quite satisfactory for bleaching and for use in the determination of bleach index of lac. The stability of a typical sample of bleach liquor so prepared and preserved in glass stoppered brown bottles, both in a refrigerator (3°-5°C.) as well as at room temperature, is indicated in Table 4.

Influence of free alkalinity of the bleach liquor on the results of the bleach test — It has been recognized that excessive alkalinity in the bleach liquor introduces errors in bleach tests. But no attempt appears to have been made to fix the permissible range of alkalinity. The present investigations have conclusively shown that bleach liquors of free alkalinities within the range of 0·02-0·04N are quite satisfactory. In order to determine the variation in the values of bleach index with the free alkalinity of the bleach liquor, the bleach index of the same sample of seedlac was determined using bleach liquors containing different amounts of free alkali. The results are given in Table 5.

By plotting the bleach index values against the free alkali content of the bleach liquor (Table 5), a curve (Fig. 1) is obtained from which it is clear that practically constant values for bleach index are obtained up to a maximum free alkalinity of about 0·04N, and above this figure, the value of bleach index rises rapidly with increase in free alkalinity.

End-point of bleaching — No uniform procedure is followed for fixing the end-point of bleaching nor is there any agreed standard for the end-colour of bleached lac solution. This is partly because a uniform reproducible shade cannot be ensured for every type of lac to be bleached, and consequently the value of bleach index or bleachability has often to be supplemented

TABLE 4 — STABILITY OF SODIUM HYPOCHLORITE SOLUTION OF FREE ALKALINTY 0·032N

Time of storage months	Available chlorine in sample kept in	
	Refrigerator (3°-5°C.) %	Room temp. (20°-30°C.) %
Freshly prepared	6·137	6·137
1	6·095	5·813
2	6·061	5·449
6	5·954	4·815

TABLE 5 — BLEACH INDEX OF THE SAMPLE OF SEEDLAC USING BLEACH LIQUORS CONTAINING DIFFERENT AMOUNTS OF FREE ALKALI

Normality of free alkali	Colour ratio	Bleach index
0·0144	1·800	100
0·0296	1·960	97
0·0353	1·990	96
0·0642	1·725	101
0·1534	1·180	113
0·3602	0·340	145

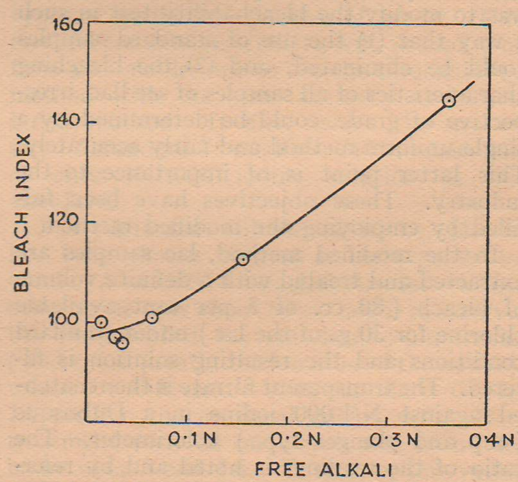

Fig. 1—Free alkali content of bleach liquor vs. bleach index

by remarks on the shade or colour of the bleached lac solution eventually obtained.

In the method used by Messrs Angelo Bros. Ltd., Calcutta, the *speed* of absorption of bleach liquor is made use of in ascertaining the end-point. A sample is considered to have been fully bleached when 5 cc. of standard bleach are not consumed within 90 min. under the given conditions. In Sen's modified method[20], bleaching is assumed to be complete when the colour of the wax-free solution matches that of N/2,000 iodine solution.

In the United States Shellac Importers' Association (USSIA) method for bleach index the comparison of end-colour is made with the suspended wax particles against that of a standard seedlac bleached simultaneously. For these tests, therefore, standard seedlacs are essential.

In the recently introduced bleachability test of the USSIA, the sample is treated with a definite volume of bleach, namely 80, 100, 115 or 140 cc., depending upon the grade of seedlac used, and the end-colour is compared with that of standard seedlacs which are simultaneously bleached under identical conditions.

The bleachability test is an improvement over the existing bleach index methods, but it still suffers from two shortcomings: (1) standard seedlac samples are needed, and (2) the results are relative and are expressed in terms of " equal to " or " lighter than " or " darker than " the standard.

The object of the present investigation was to modify the bleachability test in such a way that (1) the use of standard samples could be eliminated, and (2) the bleaching characteristics of all samples of seedlac, irrespective of grade, could be determined by a single uniform method and fairly accurately. This latter point is of importance to the industry. These objectives have been fulfilled by employing the modified method.

In the modified method, lac samples are extracted and treated with a definite volume of bleach (80 cc. of 3 per cent available chlorine for 30 g. of the lac) under standard conditions and the resulting solution is filtered. The transparent filtrate is then matched against N/1,000 iodine in a Dubosque (cup and plunger type) colorimeter. The ratio of the readings is noted and by reference to the curve (FIG. 2) the bleach index of the sample is found out.

Procedure — Seedlac is coarsely powdered so as to pass through a 10-mesh sieve and rolled on paper to ensure uniformity. Seedlac ($37{\cdot}5 \pm 0{\cdot}1$ g.) and anhydrous sodium carbonate ($3{\cdot}7 \pm 0{\cdot}1$ g.) are weighed into a 400 cc. tall beaker and mixed up with 110 cc. of hot water at $70° \pm 2°$C. The beaker with its contents is then quickly transferred to a boiling water bath. The contents of the beaker are kept stirred with a glass rod by hand, vigorously at first, till the initial frothing is over and thereafter only occasionally. After exactly half an hour the beaker is removed from the water bath and 25 cc. of hot water ($70° \pm 2°$C.) are run down the sides of the beaker. The extract is then well mixed and immediately strained through a copper or brass 100 mesh wire-gauze filter into a 500 cc. graduated cylinder. The beaker and the residue are washed with hot water at $70° \pm 2°$C. taking care that the filtrate (including washings) does not exceed 250 cc. The extract is then cooled to room temperature in a stream of running water and made up to 280 cc. with distilled water. It is then drained into a 400 cc. tall beaker and mixed with 95 cc. of bleach liquor having an available chlorine content of $3 \pm 0{\cdot}05$ per cent. The solution is occasionally stirred with a glass rod during the next half an hour and then allowed to stand overnight in a dark place, preferably at about $27° \pm 2°$ C. Next morning the wax collecting on the surface is cautiously stirred into the solution by means of a glass rod without disturbing any sediment present. Exactly 300 cc. of the sediment-free supernatant solution are then measured and poured into a 400 cc. beaker and treated with an additional 4 cc. of the bleaching agent. The solution is mixed well and allowed to stand for half an hour. A small portion is then filtered, through a dry filter paper, the first 1 or 2 cc. of the filtrate being rejected, as this is likely to be cloudy. The colour of the subsequent clear filtrate is then determined by matching against N/1,000 iodine in potassium iodide solution in Dubosque colorimeter.*

*It has been ascertained experimentally that no change of colour takes place during filtration of the wax and that the results of colour comparisons of bleached lac solutions are practically the same irrespective of whether the comparisons are carried out visually in the presence of the full complement of wax or colorimetrically after filtering off the wax.

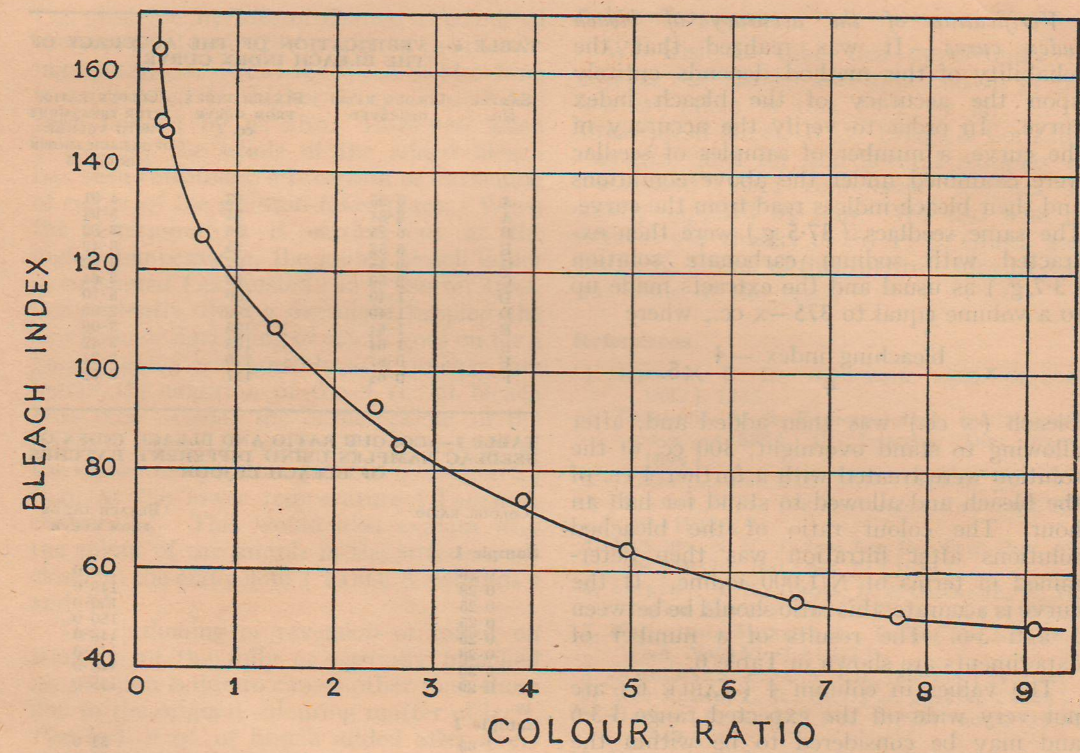

FIG. 2 — COLOUR RATIO VS. BLEACH INDEX

The ratio of the length of the column of the filtered bleached solution to that of the column of the iodine is indicative of the bleach index of the sample. For example, with seedlacs of a bleach index of 80 cc. this value is found to be between 3 and 3·6. Obviously for any sample, the bleach index of which is higher, this ratio will be smaller because the solution would have been only partially bleached in view of the insufficiency of bleach. Conversely, for a sample of a bleach index lower than 80 the ratio will be higher as the sample would have been over-bleached.

From this simple relationship the bleach index of any sample is easily determined. A number of seedlac samples of known bleach indices were examined under the above conditions using a total of 80 cc. of bleach liquor for 30 g. of the sample. A curve (FIG. 2) was drawn by plotting the colour ratio against the bleach index of the respective samples. To determine the bleach index of any unknown sample, it is only necessary to determine the colour ratio under the conditions described above. The bleach index may then be directly read from the curve. The procedure is universal and applicable to all types of seedlac irrespective of grade. This method combines simplicity with economy of time and enables one to use the bleachability method with the same accuracy as bleach index method. It also avoids the use of any " standard " seedlac and makes use of only N/1,000 iodine solution as the standard.

The particular volume of 80 cc. bleach has been chosen because it corresponds to Grade 1A of USSIA bleachability test. Any other value near about 80 cc. might also serve the purpose but the standard colour ratio (and consequently the location of the curve) would be different. With standard Grade 1A seedlac the eventual colour ratio after treatment with 80 cc. bleach was found to be between 3 and 3·6. Therefore, this value has been taken to be the standard for an adequately bleached sample.

Verification of the accuracy of bleach index curve — It was realized that the reliability of this method depends entirely upon the accuracy of the bleach index curve. In order to verify the accuracy of the curve, a number of samples of seedlac were examined under the above conditions and their bleach indices read from the curve. The same seedlacs (37·5 g.) were then extracted with sodium carbonate solution (3·7 g.) as usual and the extracts made up to a volume equal to 375—x cc., where

$$x = \frac{\text{bleaching index} - 4}{4} \times 5.$$

Bleach (x cc.) was then added and, after allowing to stand overnight, 300 cc. of the solution were treated with a further 4 cc. of the bleach and allowed to stand for half an hour. The colour ratio of the bleached solutions after filtration was then determined in terms of N/1,000 iodine. If the curve is accurate, this ratio should be between 3 and 3·6. The results of a number of experiments are shown in Table 6.

The values in column 4 (Table 6) are not very wide off the expected range 3-3·6 and may be considered to be within the limits of experimental error.

Reproducibility of the results — Many seedlac samples were examined by the above method using the same as well as different batches of bleach liquor. Concordant results were obtained as shown in Table 7 for two typical samples.

Effect of temperature — Temperature has considerable influence on the speed of hypochlorite bleaching. It was, therefore, considered necessary to determine how far the results obtained by the improved method are affected by the temperature at which bleaching is carried out. With this end in view, the determinations were carried out on a number of seedlac samples, the solution in contact with the bleach liquor being allowed to stand overnight (1) at the laboratory temperature (30°-35°C.), (2) in a refrigerator at 3°-5°C., and (3) in a thermostat at 35°C. The colour ratios of some of the solutions before the addition of 4 cc. of bleach were also determined. The results obtained are given in Table 8.

It is evident from the figures in Table 8, columns 4, 5 and 6, that varying the temperature from 3° to 35°C. has no appreciable effect on the results obtained in the bleaching experiments. This observation may, at first sight, appear to be surprising, but the following considerations provide a satisfactory explanation.

In the bleaching process two factors play an important role: (1) the speed of bleaching

TABLE 6 — VERIFICATION OF THE ACCURACY OF THE BLEACH INDEX CURVE

Sample No.	Colour ratio observed	Bleach index from curve cc.	Colour ratio after treatment with volume of bleach shown in col. 3
A	3·95	73	4·01
A	3·84	74	3·94
B	6·25	56	3·82
B	6·52	55	3·42
C	2·45	92	3·92
C	2·50	92	3·64
D	1·40	109	3·70
D	1·40	109	2·96
E	1·64	105	3·09
E	1·64	105	3·42
F	0·87	120	3·34
F	0·64	127	3·62

TABLE 7 — COLOUR RATIO AND BLEACH INDEX OF SEEDLAC SAMPLES USING DIFFERENT BATCHES OF BLEACH LIQUOR

Colour ratio	Bleach index from curve
Sample 1	
0·26	150·0
0·28	148·0
0·25	150·0
0·25	150·0
0·29	148·0
0·28	148·0
0·30	148·0
0·29	148·0
Sample 2	
7·69	51·0
6·66	54·0
6·58	54·5
6·59	54·5
6·73	54·0

TABLE 8 — COLOUR RATIOS OF DIFFERENT SEEDLAC SOLUTIONS

Sample	Before addition of final 4 cc. of bleach		½ hr. after addition of final 4 cc. bleach		
	30°-35°C.	3°-5°C.	30°-35°C.	3°-5°C.	35°C.
P	4·30	4·56	5·64	5·32	—
Q	—	2·61	3·12	2·64	—
Q	0·81	2·91	2·77	2·94	—
R	1·24	3·48	4·27	4·27	—
S	0·51	1·05	1·39	1·41	—
S	0·45	1·22	1·25	1·44	—
S	0·56	1·40	1·47	2·19	—
T	2·24	6·24	8·84	8·90	—
T	1·98	7·44	8·98	8·94	—
A	—	—	3·40	3·49	3·40
B	—	—	3·35	3·49	3·37
C	—	—	2·74	3·06	2·75
D	—	—	0·95	0·88	0·80
E	—	—	3·00	3·48	3·52
F	—	—	3·17	3·24	3·00

(as observed by rate of change of colour of the solution), and (2) duration of the bleaching operations. That the speed of bleaching is accelerated by higher temperature[23] has been noticed by us also. However, when practically the whole of the added bleach has been consumed, a reversion or darkening of colour of the solution takes place. When the determination is carried out at the higher temperature, the added bleach liquor is consumed (exhausted) in a shorter time. Consequently, during overnight keeping the reversion or darkening of colour goes on for a longer period and possibly at a quicker rate before the addition of the 4 cc. of bleach next day. Hence the darker colour of the solution which is maintained overnight at the higher temperature (TABLE 8, column 2) than at the lower temperature (TABLE 8, column 3). This would also explain why the colour of the sample in the latter case is closer to the end-colour (TABLE 8, columns 4 and 5).

The darkening or reversion of colour on standing of the fully or partially bleached lac solution is due to causes other than those due to the original colouring matter of lac[24]. The final 4 cc. of bleach added after overnight standing helps to discharge only the colour regained. The solution is thereby brought back to the same colour which it had when bleaching was complete and the darkening had not commenced; in other words, to the same colour the bleached solutions would have had if there had been no darkening. This should naturally depend only upon the *amount* of bleach used and not on the *temperature* of bleaching although the time required to reach this stage may be shorter at higher temperatures than at lower temperatures.

Determination of the bleach index of a number of samples by the method described above was made not only by one of the authors (Y.S.) but also by junior workers in this Institute and no difficulty whatsoever was experienced by them in obtaining consistent and satisfactory results.

Acknowledgement

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