Note on the Improvement of Color in Off-Colored Cottonseed Oils[1]

The alkali-fast red and orange coloration that occurs in cottonseed oil is of an undesirably high intensity in about one-fourth of the domestic production. A part of this coloration can arise from gossypol that is incorporated into the oil during the processing of cottonseed at the oil mills. This possibility has been established by Berardi and Frampton (1), who showed that a comparable alkali-fast coloration develops when gossypol is added either to a refined, bleached, and deodorized cottonseed oil or to synthetic tripelargonin.

An inference, which may be drawn from several observations, is that the chromogen in the off-colored oils is quinoid in nature. Although quinoid derivatives of gossypol that may arise in off-colored cottonseed oils have not been isolated or synthesized, the evidence from studies on the chemical behavior of gossypol suggest that gossypol, and possibly gossypol derivatives, can be converted into ortho quinones. These substances would be expected to be red in color. It has been demonstrated in this laboratory, for example, that gossypol, in an alkaline medium and in the presence of molecular oxygen, participates in the Strecker degradation of amino acids. The implication is that gossypol is converted into a product having the grouping $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$ since this grouping is essential to the degradation (2).

The assumption that the chromogenic materials in off-colored cottonseed oils are quinoid in character has formed the basis of the efforts recorded here to improve upon the color. The objective has been that of inducing high-polymer formation, in either crude or refined cottonseed oils, through the use of polyfunctional reagents that will form adducts with carbonyl compounds. The more successful of the experiments have been those in which polyfunctional aliphatic amines were used. Success has been achieved in the efforts to improve upon the color of every cottonseed oil studied when diethylenetriamine was used.

Experimental

Off-colored solvent hydraulic and screw-press oils were used. The same laboratory-scale refining and bleaching procedure was used in all of the experiments recorded, except for the variations in the quantities of amine or alkali used. The following steps constitute the procedure.

A. *Treatment.* Two hundred grams of crude oil are weighed into a 400-ml. beaker, and the required amount of amine is added. The mixture is stirred well for a few minutes and drained into four 100-ml. capacity centrifuge tubes. The material is centrifuged at high speed (6,000 r.p.m.) for 10 min. and drained into the tared container of a standard blender.

B. *Refining.* Three-fourths of the amount of alkali specified in the official A.O.C.S. methods (3) is added to and mixed with the oil in the blender, after which the mixture is drained into a tared stainless steel refining cup. The entrainment loss should be approximately 1.0 g. The oil-alkali mixture is then stirred in a water bath (60°C.) for 5 min. and drained into four 100-ml. capacity centrifuge tubes. The entrainment loss should be approximately 0.2 g. at this point. The mixture is centrifuged at high speed (6,000 r.p.m.) for 10 min. and then drained into a tared stainless steel refining cup. The amount of oil recovered at this stage will depend upon the amount and strength of the alkali added.

C. *Bleaching.* Next 4.67% of A.O.C.S. Official Natural Bleaching Earth (3) are added to the recovered oil, and the resulting suspension is then stirred and heated according to conventional procedures (3). The mixture is drained into four 100-ml. capacity centrifuge tubes and centrifuged at high speed (6,000 r.p.m.) for 10 min. The amount of oil recovered at this stage and the original weight of oil sample (200.0 g.) are used to calculate the percentage of loss after bleaching.

The color is determined as directed in A.O.C.S. Tentative Method Cc 13c-50 (Photometric Method) (3).

Results and Discussion

No procedure has been developed for determining the quantity of amine required for the different off-colored cottonseed oils. It was established empirically that a quantity of amine equal to 2%, by weight of the oil, was essential for a maximum improvement of oil color in the experiments with crude cottonseed oils reported in this communication. The use of larger quantities of amine did not result in a further improvement in color.

TABLE I

Improvement in Color of Off-Colored Cottonseed Oil (Screw-Press Oil) Through the Use of Diethylenetriamine

Quantity of amine expressed as % of oil	Quantity of NaOH per 100 g. of oil used in refining step	% refining loss	Color of finished oil
0	1.5	18.7	7.1[a]
0	1.1	14.9	9.3
1	1.1	14.8	3.4
2	1.5	17.1	2.1
2	1.1	16.1	1.9
2.5	1.1	18.1	1.8

[a] Refined and bleached in accordance with standard procedure.

Data recorded in Table I were obtained with an off-colored screw press oil. It will be noted that marked improvement in color was obtained when diethylenetriamine was used as the reagent, *e.g.*, the observed photometric reading was reduced from a value of 7.1 for the control oil [refined and bleached in accordance with the official methods of the American Oil Chemists' Society (3)] to a value of 1.8 when the amine was used in the refining and bleaching procedure.

The data recorded under "Control, Bleached Oil Color" in Table II were those obtained through the use of the conventional refining and bleaching procedures; those recorded under "Treated, Bleached Oil Color" were obtained by the addition of the amine to the crude oil.

TABLE II

Effect of Diethylenetriamine on Cottonseed Oil Color

Source of oil	Control		Treated		Remarks
	% refining loss	Bleached oil color	% refining loss	Bleached oil color	
Solvent oil	10.3	3.9	9.4	1.5	
	10.2	7.4	10.5	3.1	3 mo. later stored in laboratory
Screw-press oil	18.7	7.1	16.1	1.9	
	18.7	7.1	14.0	2.5	Used 50% the amount of alkali recommended by A.O.C.S. for refining
Hydraulic oil	9.8	3.5	8.8	1.8	
	10.8	5.3	9.5	1.7	
Commercial cottonseed oil (refined, bleached, deodorized, and winterized) plus gossypol	4.3	7.2	4.3	3.0	

It may be noted that, while oil color was improved by the addition of the amine to the oil after the refining step and before the bleaching operation, it was not as great as when the amine was added to the crude oil. The reason for this is not understood.

Attention is directed to the last item in the table. The off-colored cottonseed oil that was prepared by the addition

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[1] Presented at the American Oil Chemists' Society Meeting, New Orleans, Louisiana, April 29–May 1, 1957.

of gossypol to a refined, bleached, and deodorized cottonseed oil and that was unbleachable by the conventional procedures responded to the treatment with diethylenetriamine. The fact that the red colors in some of the oils studied are not eliminated suggests that there are more than one color bodies in these off-colored oils.

The best results were obtained with diethylenetriamine, but other aliphatic polyfunctional amines yield good results. A comparison of the relative effectiveness of several amines is tabulated (Table III). The effects of some amines were deleterious.

TABLE III

Effect of Amines on Cottonseed Oil Color (Solvent Oil)

Amine used	Quantity of amine used (%)	Quantity of NaOH in g. per 100 g. oil in refining step	Refining loss (%)	Color of finished oil
Control	....	0.64	10.2	7.4 [a]
Control	....	0.58	10.8	7.7
Aniline	2	0.59	6.2	13.4
n-Octadecylamine	5	0.56	13.5	21.7
o-Phenylenediamine	2	0.58	10.7	12.4
Polyglycolamine H-163 [b]	2	0.48	10.4	3.9
N-Aminoethylethanolamine	2	0.48	10.8	4.2
Diethylenetriamine	2	0.64	12.7	3.1
Diethylenetriamine	2	0.48	10.5	3.1
Triethylenetetraamine	2	0.48	10.8	3.9
Tetraethylenepentaamine	2	0.48	10.1	3.6

[a] Refined and bleached according to the A.O.C.S. official methods.

[b] α(1-aminopropoxy)–β'–hydroxydiethyl ether or $HOCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2NH_2$

The combination of the amines with the chromogenic materials in the oils is extremely rapid so that the residence time of the amine in the oil may be short enough so that aminolysis of the glycerides is insignificant. This aminolysis is rapid, and crystals of the fatty acid amides are apparent in the oils in a few hours if the residence of the amines in the oil is prolonged. The amines are removed from the oil in the bleaching clay.

Discussion

Incorporation of polyfunctional aliphatic amines into the procedure for refining cottonseed oil improves the color of the refined and bleached oil. This is accomplished in the laboratory without any increase in refining loss. Such results would suggest that it may be possible to modify the refining procedure in a practical way to obtain lighter-colored oils and hence to eliminate the problem of color in cottonseed oil. While proposals to modify the refining of vegetable oils have been made from time to time, the basic process has remained unchanged; caustic soda and soda ash are still the refining agents of choice.

The introduction of the use of aliphatic amines in the refining and bleaching of cottonseed oils will necessarily depend upon the results obtained from further study. For example, evidence will have to be presented that the quality and stability of the oil are not impaired by the amine treatment, and it must be demonstrated that all traces of the amines are removed during the processing. In addition, engineering and economic factors have not been evaluated.

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REFERENCES

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Meeting Calendar . . .

August 18, 1958 — National Soybean Processors Association, Hotel Fort Des Moines, Des Moines, Ia.

August 19–20, 1958—American Soybean Association, 38th annual meeting, Hotel Fort Des Moines, Des Moines, Ia.

August 25–29, 1958—Infrared Spectroscopy Institute, second annual institute, Canisius College, Buffalo, N. Y.

September 4–6, 1958—The Chemical Institute of Canada, fourth western regional conference, University of Manitoba, Winnipeg

September 7–20, 1958—Société de Chimie Industrielle, 31st international congress of industrial chemistry, Liége, Belgium

September 9–12, 1958—American Chemical Society, 134th national meeting, and National Chemical Exposition, Chicago, Ill.

September 15–19, 1958—Instrument Society of America, 13th annual instrument-automation conference and exhibit, Philadelphia, Pa.

September 22–24, 1958—Standard Engineers Society, seventh annual meeting, Benjamin Franklin hotel, Philadelphia, Pa.

September 23–25, 1958—International Society for Fat Research, third congress, Seville, Spain

October 5–8, 1958—Federation of Paint and Varnish Production Clubs, 36th annual meeting and 23rd Paint Industries' Show, Cleveland Public Auditorium, Cleveland, O.

October 6–8, 1958—National Association of Corrosion Engineers, northeast regional conference, Boston, Mass.

October 20–24, 1958—National Association of Corrosion Engineers, south central regional conference, New Orleans, La.

October 22–24, 1958—American Vacuum Society, fifth national vacuum symposium, Sir Francis Drake hotel, San Francisco, Calif.

November 18–20, 1958—American Standards Association, ninth annual conference on Standards, Roosevelt hotel, New York, N. Y.

Anderson Is Consultant for New Canadian Plant

The V. D. Anderson Company, Cleveland, O., is serving as consulting firm, major equipment supplier, and manufacturer of all oil-extraction equipment for a plant now under construction in Alberta by the Western Canadian Seed Processors Ltd. The first such plant in Alberta, this new oleaginous seed-processing plant with complete refinery and hydrogenation equipment will cost an estimated $2,700,000 and will have a capacity for processing 200 tons of sunflower seed or 115 tons of flaxseed per 24-hr. day.

The area from which the company will obtain raw materials for processing includes nearly all of southern Alberta. Processing of safflower, rapeseed, and soybeans is being considered for a later date.

Fatty Acids Drop

Production of fatty acids in May 1958 totalled 30.9 million lbs., slightly below the April level, according to the Fatty Acid Producers' Council. Production of types reported last year (without fatty acids from tall oil) was 25.4 million lbs. in May 1958 as compared to 34.6 million for the same categories in 1957.

The production of fatty acids from tall oil in the less-than-2%-rosin category was 5.5 million lbs. as compared to 5.2 million in April.

Total fatty acid disposition in May was 34.4 million lbs., of which 7.0 million were fatty acids from tall oil. Disposition of types reported last year was 27.3 million lbs. in May 1958 as compared to 34.8 million in 1957.

Finished goods inventories for all acids totalled 42.2 million lbs. as compared to 44.7 million at the end of April. Work-in-process stocks fell about 2.0 million lbs., with decreases occurring mainly in unsaturated fatty acids.