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Effect of Ethylene-Vinyl Acetate Copolymer-Based Depressants on the Low-Temperature Properties of Components of Light- and Heavy-Grade Marine Fuels

Natalia Kondrasheva

PhD, professor

Head of the Department of Chemical Engineering and Energy Carriers Processing

National Mineral Resources University, St. Petersburg, Russian Federation

The aim of the study

The possibility of using ethylene copolymers with vinyl acetate as additives for light and heavy distillate marine fuels for improving their low-temperature properties.

Objectives of the study

Explore susceptibility of light and heavy distillate staight-run diesel and vacuum fractions and secondary process fractions for depressant on based ethylene copolymers with vinyl acetate;

Identify optimum amount of additive for differents distillate components of marine fuel.

The use of fuels derived from paraffin-base oils is complicated by their high pour point and low mobility at low temperatures, which require the special fuel preparation systems. The mobility of such fuels at low temperatures can be improved by making their fractional composition lighter, using the expensive and energy-intensive dewaxing and hydroisomerization processes, and introducing depressants that lower the pour point of petroleum products.

When choosing depressants for various paraffinic fuels, it is necessary to consider all factors that determine their effectiveness, primarily, the chemical composition and molecular structure of the additive and the component and hydrocarbon composition of the base fuel.

Particular attention should be paid to the concentration of solid paraffin hydrocarbons in the distillate to be depressed and their melting point.

A type of effective pour-point depressants is ethylene–vinyl acetate (EVA) copolymers represented as concentrates of these products in the paraffin–naphthene fraction or in light catalytically cracked gasoil.

In this regard, a systematic study of the effect of promising copolymer depressant additives on the low-temperature properties of middle and heavy distillates, obtained via primary distillation or in secondary processes to be components of commercial marine fuels, is of great importance, as well as optimization of the composition of these additives.

Table 1. Characterizathion of vacuum gas oil from a blend of Western Siberia sour oil

Parameter	Vacuum gas oil		
	fr. 350–500°C	fr. 350–540°C	fr. 350–580°C
Density at 20°C, kg/m^3	914	921	927
Kinematic viscosity at 50°C, mm^2/s	4.55	5.71	8.90
Pour point, °C	+30	+34	+38
Sulfur content, wt %	1.62	1.65	1.80
Solid paraffins (-21°C), wt %	7.31	6.08	5.97
Melting point, °C	53	57	59

Table 2. Characterization of straight-run diesel fraction and light coker and catalytic gas oil (180-360°C) from a commercial blend of sour Western Siberia oils

Parameter	Straight-run diesel fraction	Light coker gas oil	Light cataytic gas oil
Density at 20°C, kg/m^3	838	887	864
Kinematic viscosity, mm^2/s at 20°C at 50°C	 4.46 2.41	 3.69 2.04	 3.66 2.03
Pour point, °C	–22	–34	–30
Sulfur content, wt %	0.61	1.99	0.98
Solid paraffins (-21°C), wt %	0.1	0.14	0.1

Table 3. Characterization of kerosene-gas oil fractions produced by delayed coking and catalytic cracking plants

Parameter	Coker KGO fraction (1:2 balance mixture)	Catalytic KGO fraction (2:1 balance mixture)
Density at 20°C, kg/m^3	946	874
Kinematic viscosity, mm^2/s at 20°C at 50°C	 14.46 5.28	 4.74 2.43
Pour point, °C	+10	-6
Sulfur content, wt %	2.35	1.08
Solid paraffins (-21°C), wt %	1.43	1.40
Melting point, °C	55	48

Table 4. Characterization of straight-run lube oil distillate and its extract after solvent treatment of the commercial blend of sour Western Siberia crude oils

Parameter	Extract fr. 275–400°C	Straight-run disillate fr. 275–400°C
Density at 20°C, kg/m^3	928	889
Kinematic viscosity at 50°C, mm^2/s	10.91	9.34
Pour point, °C	-4	+12
Sulfur content, wt %	2.18	1.25
Solid paraffins (-21°C), wt %	1.56	5.81
Melting point, °C	48	55

Table 5. Susceptibility of vacuum gas oils to depressant additives of set I with different amounts of VA units: A, B, C, D and E

Additive	VA,wt %	Fraction, °C	Pour point (°C) at additive content (wt %) of					ΔT,°C
			0	0.1	0.25	0.5	1.0	
A	18.8	350–500	30	16	16	22	23	14
		350–540	34	21	10	7	7	27
		350–580	38	30	30	22	26	16
B	27.0	350–500	30	23	18	8	18	22
		350–540	34	19	16	23	–	18
		350–580	38	23	21	17	19	21
C	31.4	350–500	30	24	2	5	–	28
		350–540	34	5	1	0	2	34
		350–580	38	25	14	12	12	26
D	35.4	350–500	30	6	4	-2	0	32
		350–540	34	1	0	3	–	34
		350–580	38	18	11	16	–	27
E	40.4	350–500	30	6	3	6	–	27
		350–540	34	14	6	-2	-2	36
		350–580	38	20	14	12	12	26

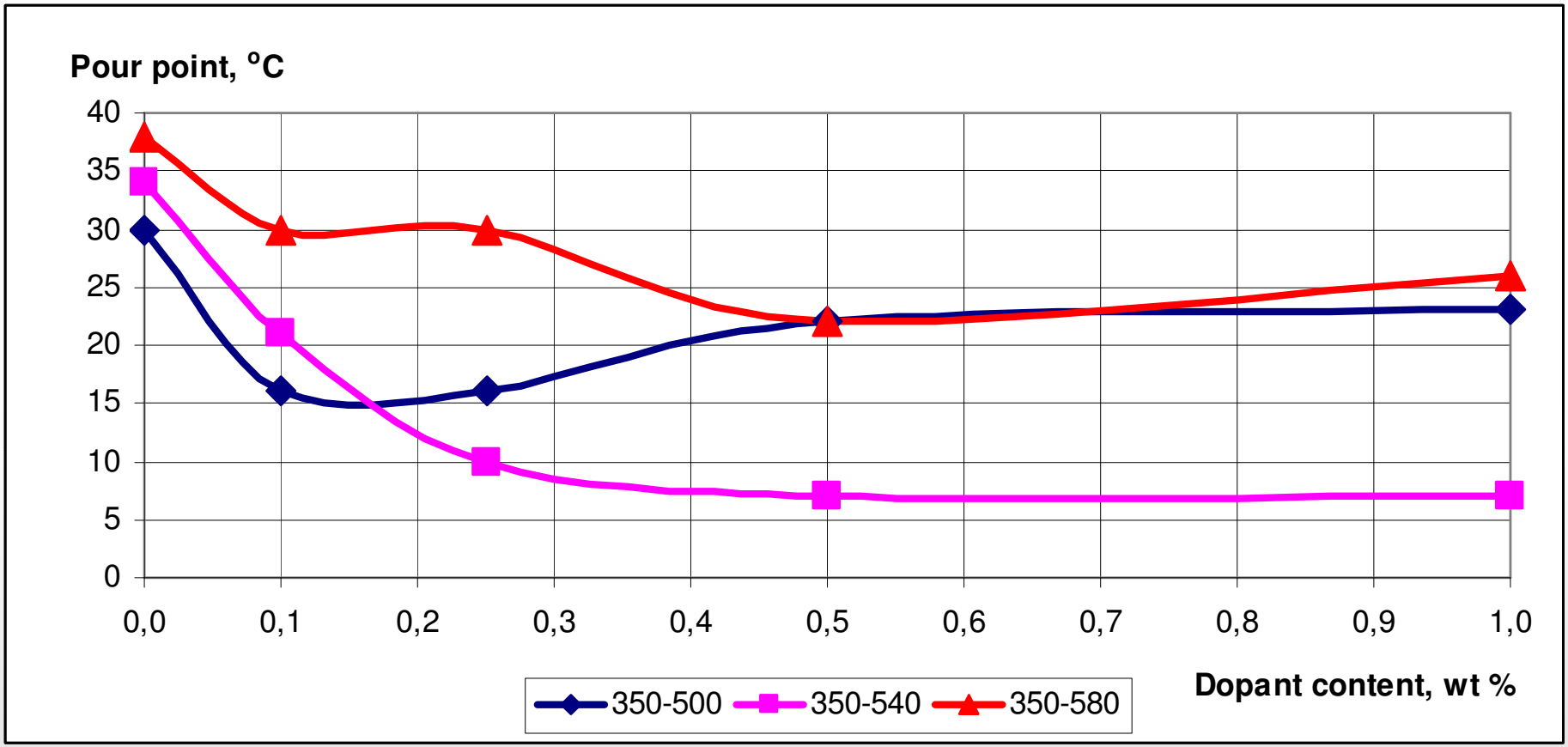


Fig. 1. Dependence of pour point of vacuum gas oil on content of dopant A: fr.350-500, fr. 350-540 and fr. 350-580

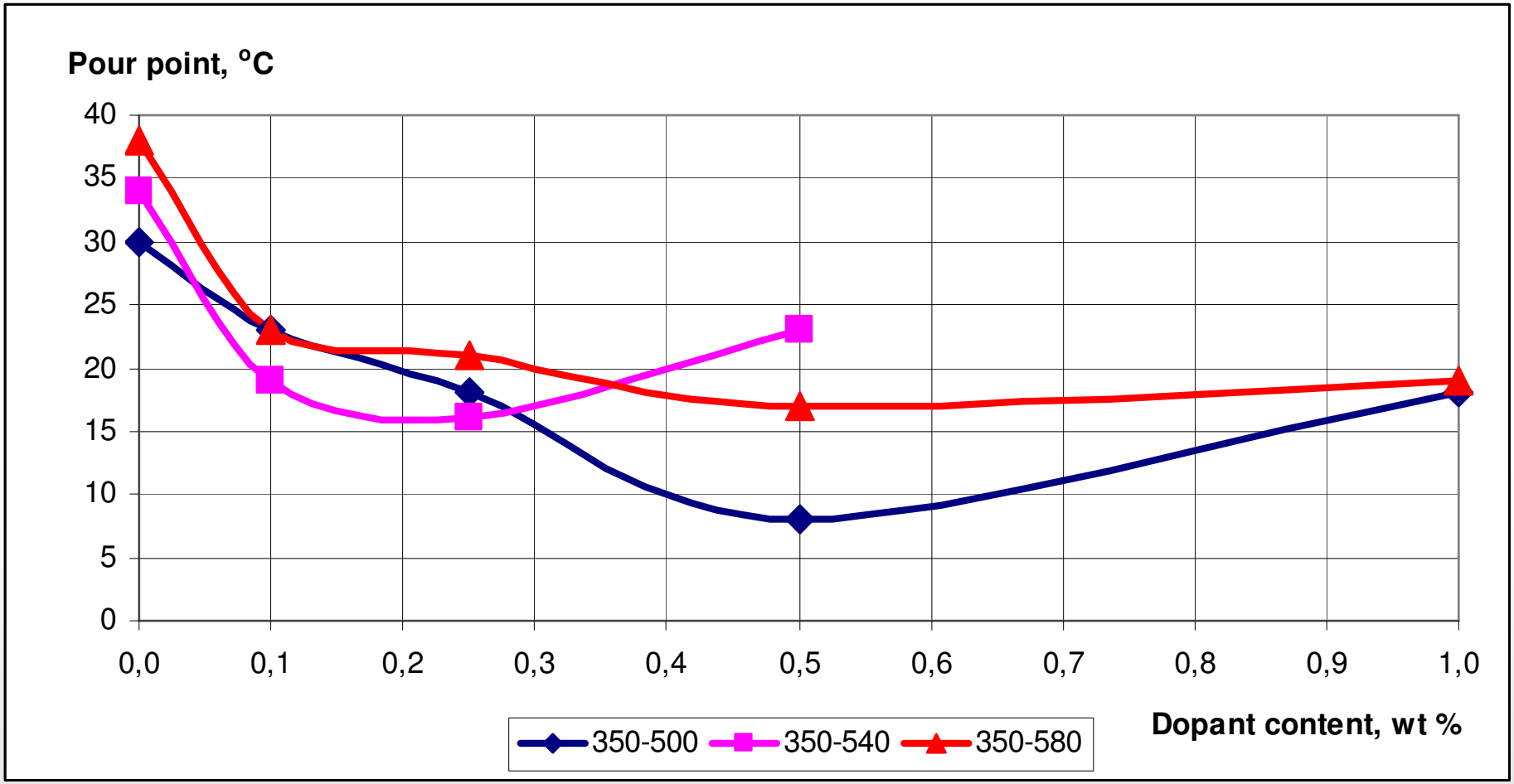


Fig. 2. Dependence of pour point of vacuum gas oil on content of dopant B: fr.350-500, fr. 350-540 and fr. 350-580

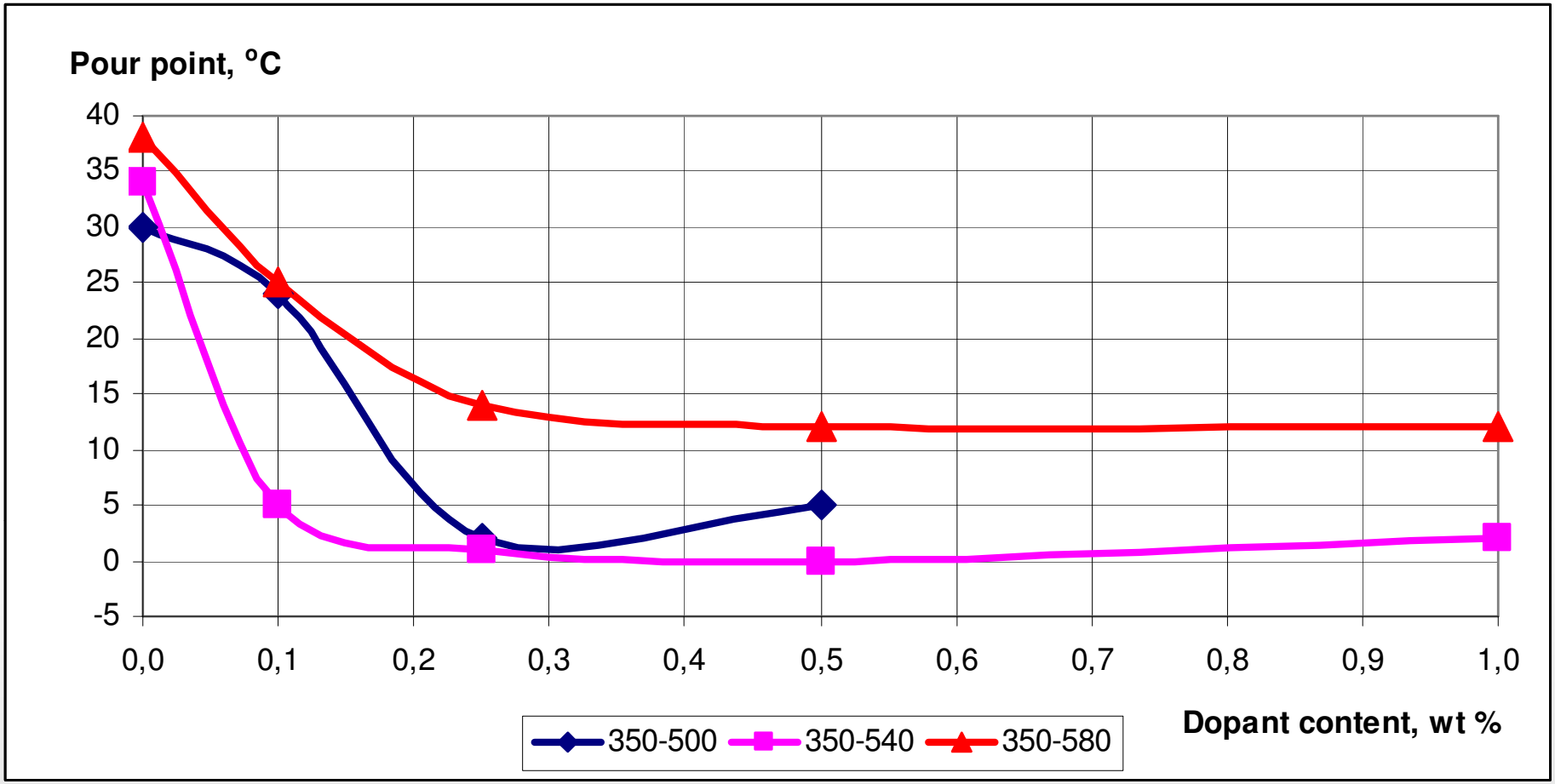


Fig. 3. Dependence of pour point of vacuum gas oil on content of dopant C: fr.350-500, fr. 350-540 and fr. 350-580

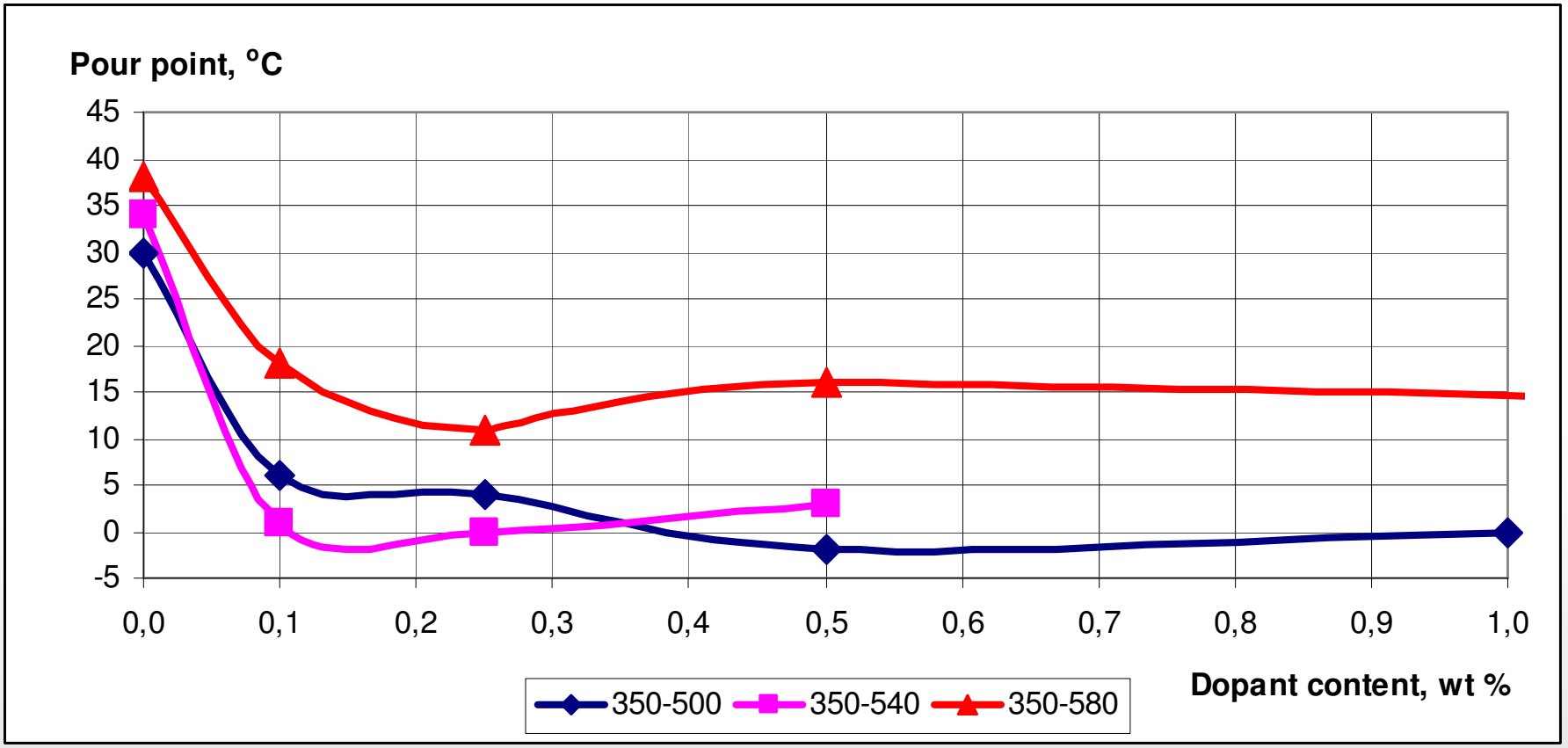


Fig. 4. Dependence of pour point of vacuum gas oil on content of dopant D: fr.350-500, fr. 350-540 and fr. 350-580

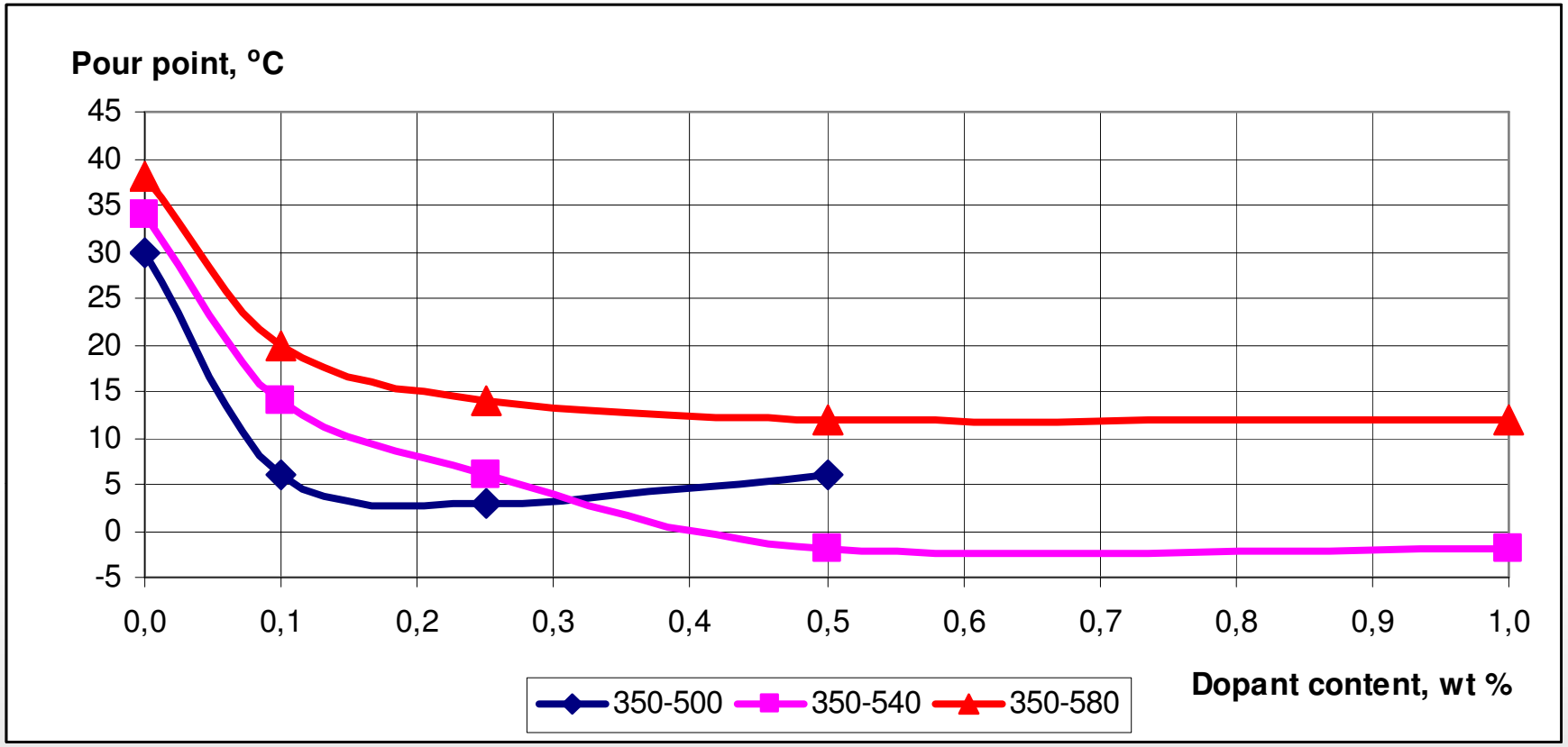


Fig. 5. Dependence of pour point of vacuum gas oil on content of dopant E: fr.350-500, fr. 350-540 and fr. 350-580

The highest depressant ability for the vacuum gas oil fractions are displayed by samples C, D and E (with a VA content of 31,4-40,4 wt %).

The highest susceptibility to pour-point depressants is exhibited by the vacuum gas oil fraction of 350-540^{o}C, which produces the maximal depression of 36^{o}C;

Table 6. Susceptibility of vacuum gas oils to depressant additives of set II (with different MFI values and an amount of VA units of 30 wt %) F, G, H, I and J

Additive	MFI	Fraction, °C	Pour point (°C) at additive content (wt %) of					ΔT,°C
			0	0.1	0.25	0.5	1.0	
F	0.08	350–500	30	30	20	22	–	10
		350–540	34	25	19	23	–	15
		350–580	38	27	23	20	26	18
G	0.7	350–500	30	9	9	6	6	24
		350–540	34	24	8	6	6	28
		350–580	38	32	19	12	12	26
H	19.2	350–500	30	19	15	8	8	22
		350–540	34	10	2	2	–	32
		350–580	38	25	18	10	12	28
I	40	350–500	30	18	5	5	–	25
		350–540	34	14	10	2	8	32
		350–580	38	32	22	24	–	16
J	87.6	350–500	30	28	26	20	24	10
		350–540	34	28	28	–	–	6
		350–580	38	34	34	–	–	4

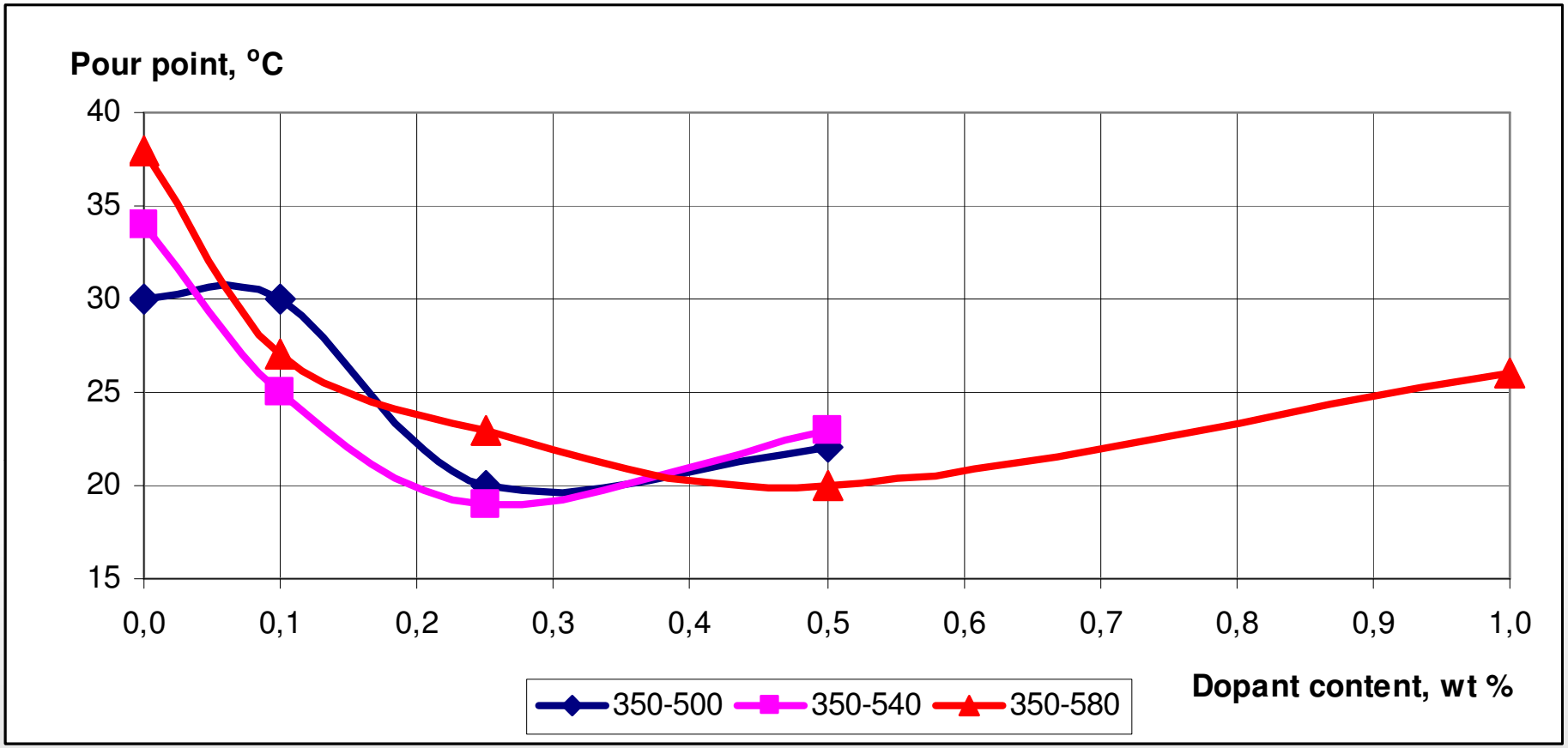


Fig. 6. Dependence of pour point of vacuum gas oil on content of dopant F: fr.350-500, fr. 350-540 and fr. 350-580

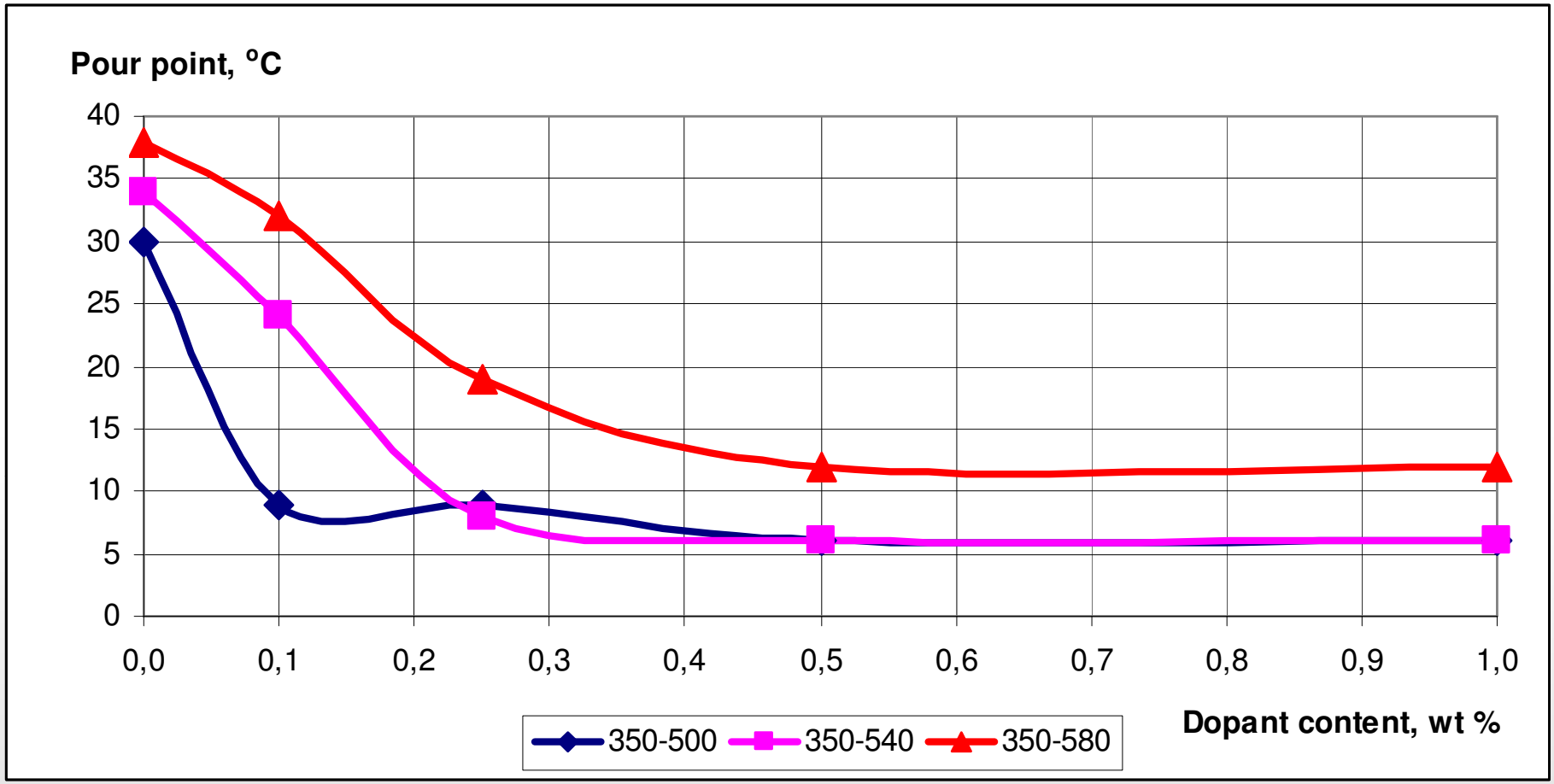


Fig. 7. Dependence of pour point of vacuum gas oil on content of dopant G: fr.350-500, fr. 350-540 and fr. 350-580

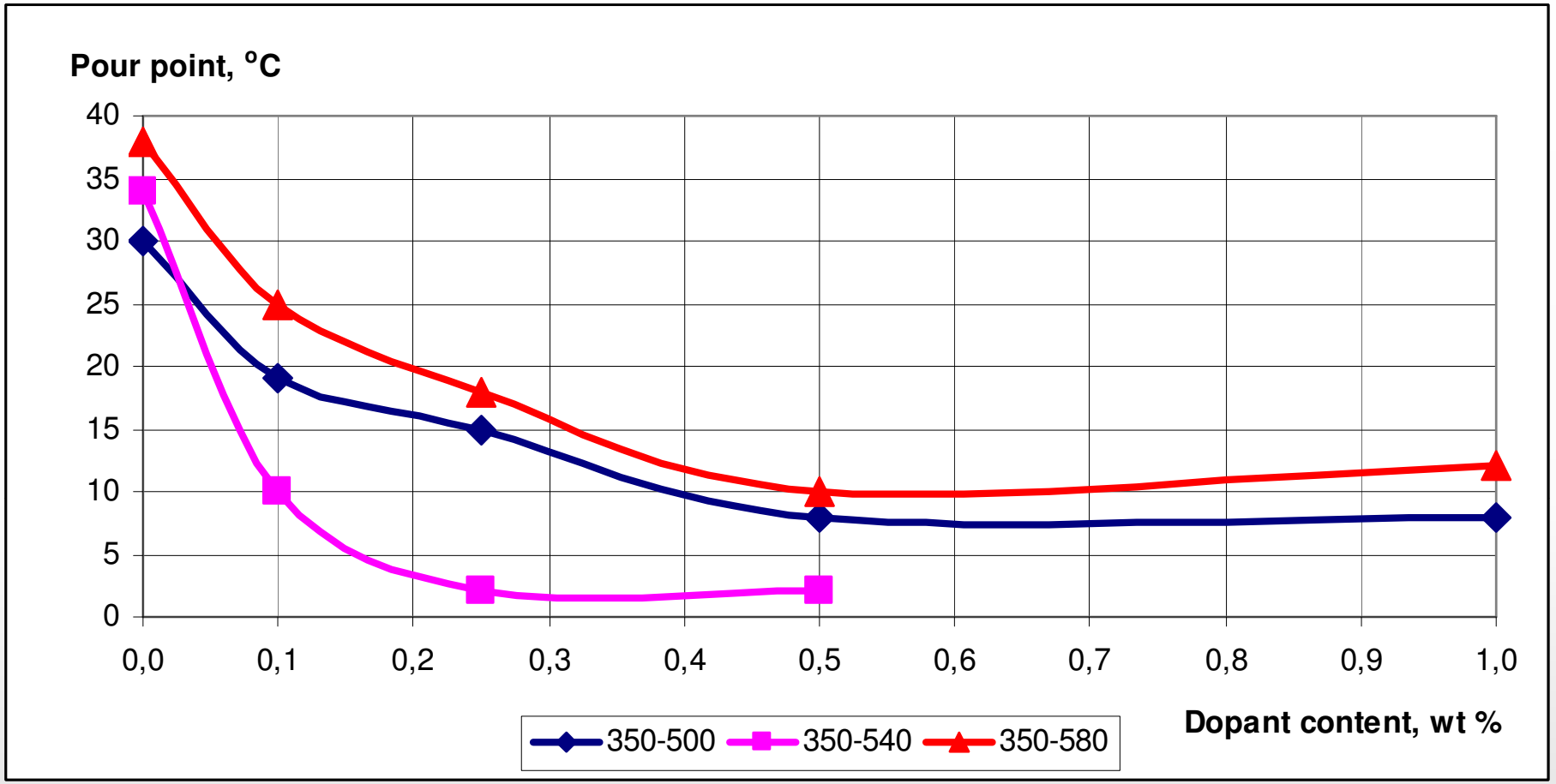


Fig. 8. Dependence of pour point of vacuum gas oil on content of dopant H: fr.350-500, fr. 350-540 and fr. 350-580

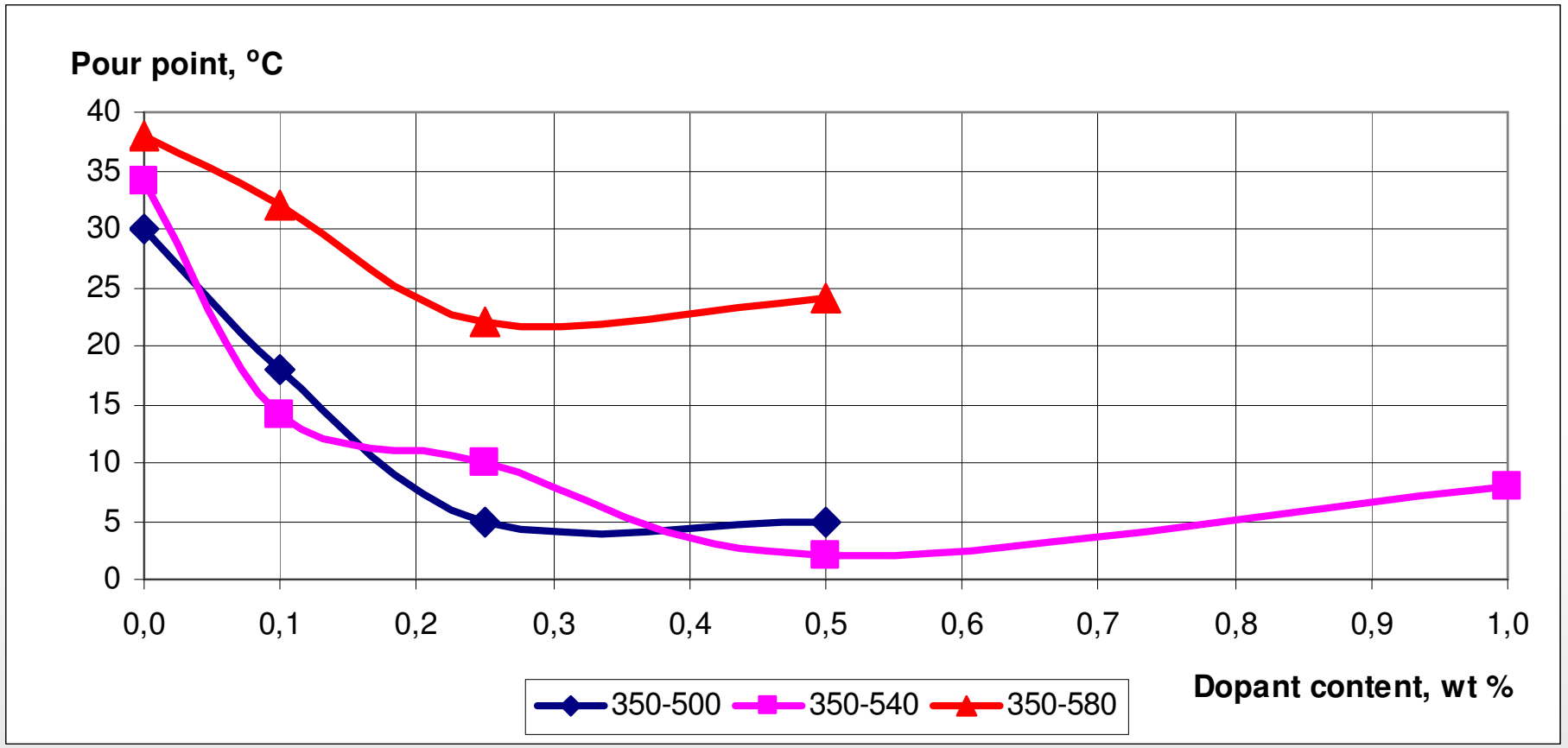


Fig. 9. Dependence of pour point of vacuum gas oil on content of dopant I: fr.350-500, fr. 350-540 and fr. 350-580

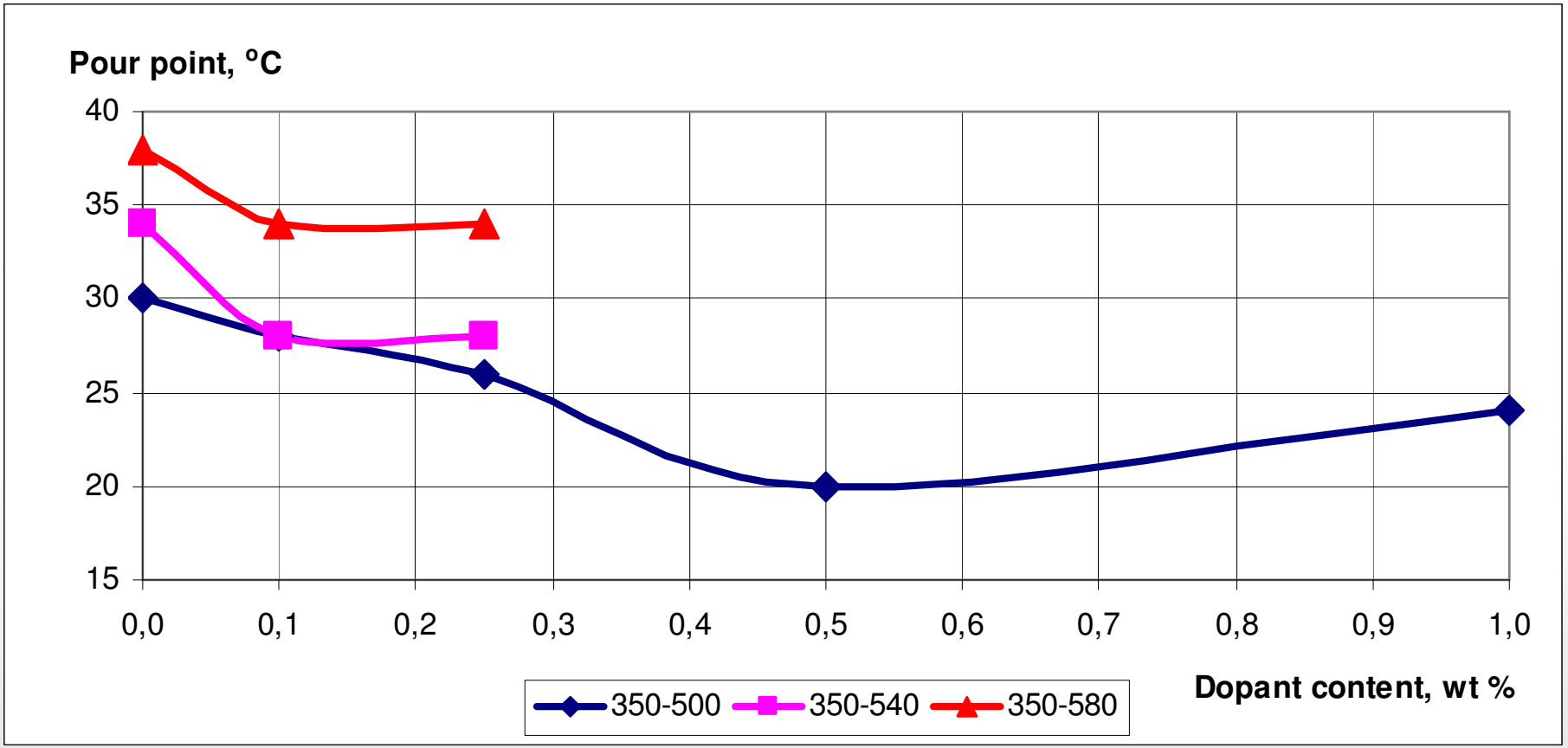


Fig. 10. Dependence of pour point of vacuum gas oil on content of dopant J: fr.350-500, fr. 350-540 and fr. 350-580

Additives G, H and I having MFI values of 0.7, 19.2 and 40.0, respectively, exibit the highest depressant ability. In this case, the vacuum gas oil fraction of 350-540^{o}C displays the highest susceptibility to these depressants: the maximum pour-point depression for this fraction is 32^{o}C.

Of the vacuum gas oil fractions examined, the 350-540^{o}C fraction having a solid paraffin content of 6.08% and a melting point of 57^{o}C exhibits the best susceptibility.

Table 7. Susceptibility of straight-run diesel fraction and light coker and catalytic gas oils to set l depressant additives (with different VA contents)

Fraction	VA,wt %	Additive	Pour point (°C) at additive content (wt %) of						ΔT,°C
			0	0.05	0.1	0.25	0.5	1.0	
Straight-run diesel reaction (180–360°C)	31.4	C	-22	-28	-30	-30	–	-	8
	35.4	D		–	-26	-30	-34	-34	12
	40.4	E		–	-26	-26	-34	-26	12
Light catalytic gas oil (180–360°C)	31.4	C	-30	-38	-54	-48	–	–	24
	35.4	D		-38	-46	-42	–	–	16
	40.4	E		-44	-40	-40	-40	-38	14
Light coker gas oil (180–360°C)	31.4	C	-34	-34	-34	-36	-36	–	2
	35.4	D		-34	-38	-34	–	–	4
	40.4	E		-	-34	-34	-34	–	0

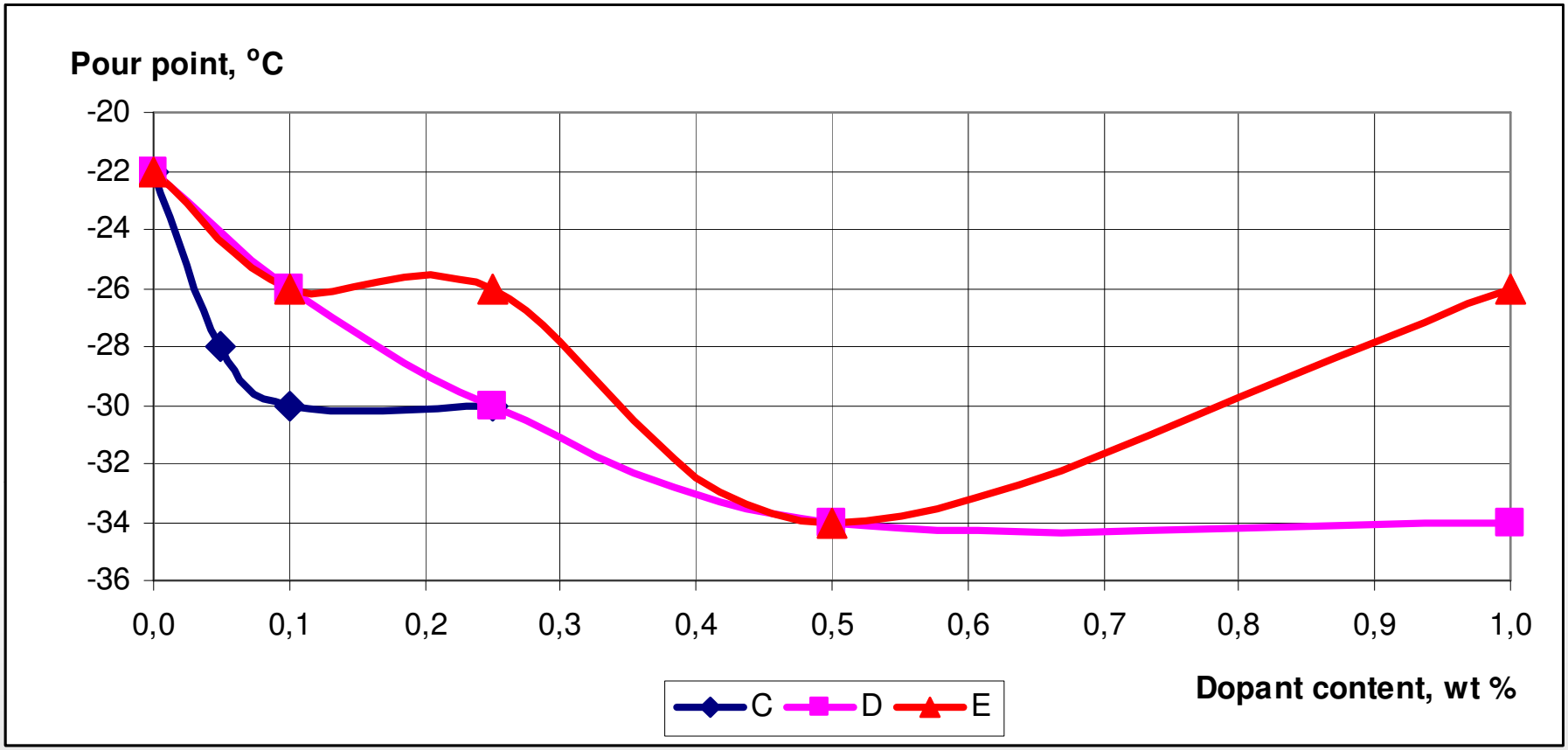


Fig. 11. Dependence of pour point of straight-run diesel reaction (180-360°C) on content of dopant C, D and E

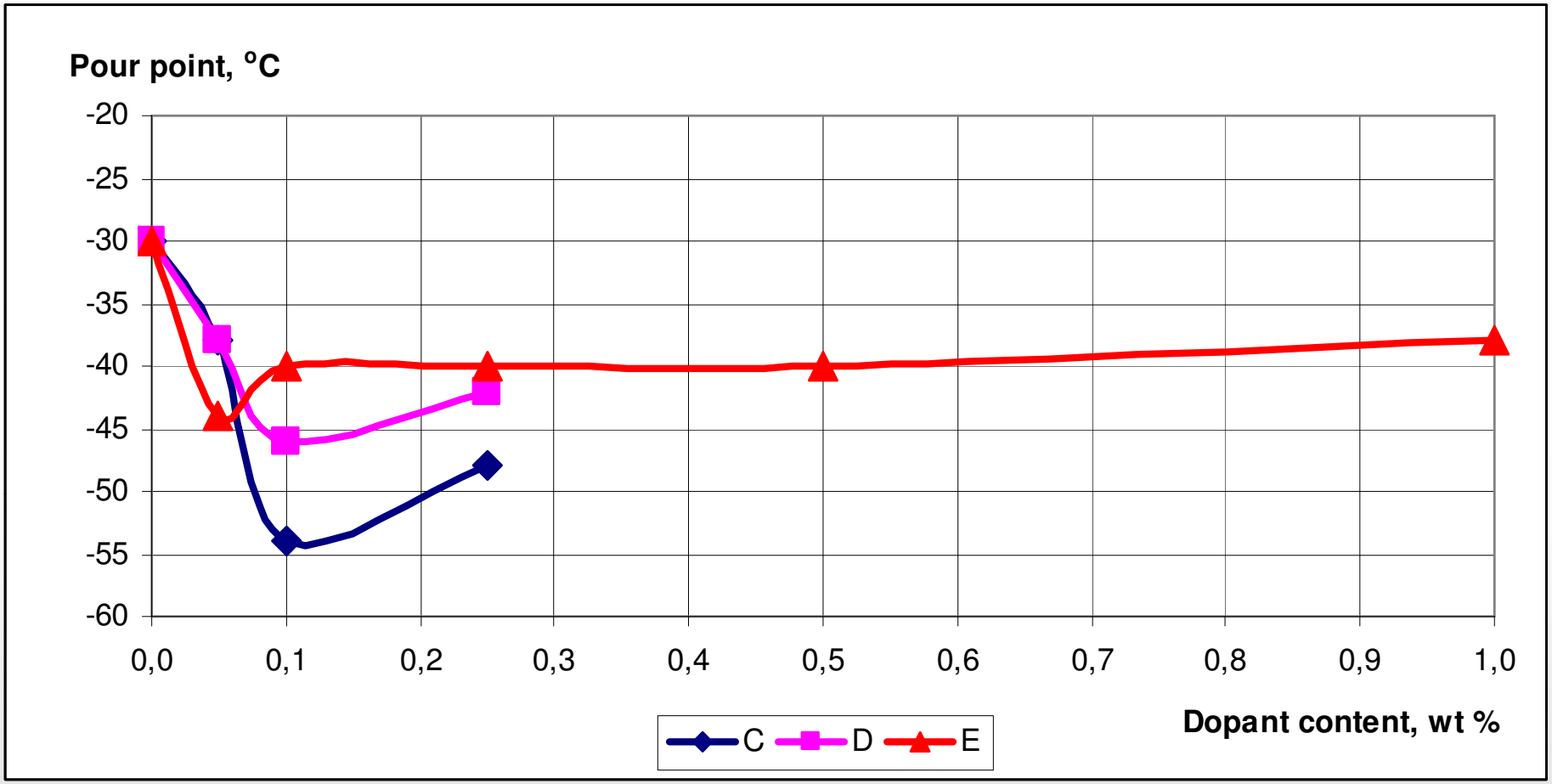


Fig. 12. Dependence of pour point of light catalytic gas oil (180-360°C) on content of dopant C, D and E

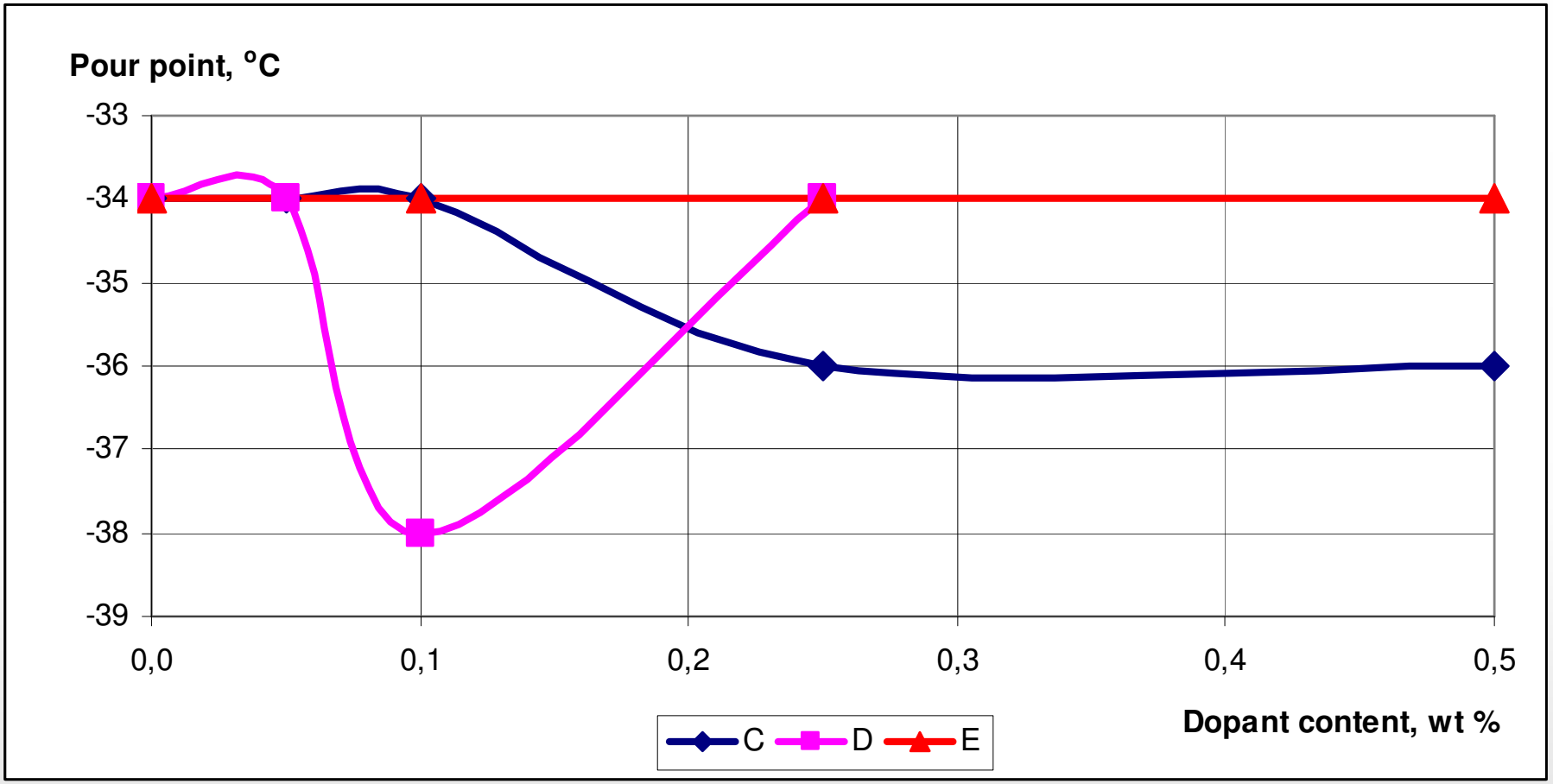


Fig. 13. Dependence of pour point of light coker gas oil (180-360°C) on content of dopant C, D and E

When set I depressants with different amounts of VA units are added to the straight-run diesel fraction, the greatest depressing effect is achieved with additives D (VA=35.4 wt %) and E (VA=40.4 wt %), which lower the pour-point of the fraction to -34°C at an optimal concentration (0.5 wt %). In the case of set II additives with different melt flow indices, the greatest depressant effect was obtained with additive I (MFI=40.0) at its concentration of 0.25-0.50 wt %;

The coker gas oil and catalytic gas oil fractions exhibit good susceptibility to the test depressants, the maximum pour-point depression is 30-40°C (40°C for the coker gas oil and 32°C for the catalytic gas oil) at an additive concentration of 0.1 wt %. The pour point of the coker gas oil was decreased from +10 to -30°C and that of the catalytic gas oil decreased from -6 to -36°C;

Table 8. Susceptibility of coker and catalytic kerosene-gas oil fractions, straight-run lube oil distillate, and its extract to set I depressant additives (with different VA contents)

Fraction	VA, wt %	Additive	Pour point (°C) at additive content (wt %) of						ΔT, °C
			0	0.05	0.1	0.25	0.5	1.0	
Coker KGO fraction	31.4	C	+10	-24	-30	-26	-26	–	40
	35.4	D		-24	-28	-24	–	–	38
	40.4	E		-24	-30	-22	-20	-18	40
Catalytic KGO fraction	31.4	C	-6	–	-34	-38	-32	–	32
	35.4	D		-36	-36	-34	-36	–	30
	40.4	E		–	-26	-28	-28	-18	22
Extract of the 275–400°C fraction	31.4	C	-4	-14	-32	-30	–	–	28
	35.4	D		–	-22	-26	-28	-26	24
	40.4	E		–	-26	-28	-26	–	24
Straight-run distillate fraction 275–400°C	31.4	C	+12	–	-16	-16	-10	–	28
	35.4	D		–	-12	-14	-18	–	30
	40.4	E		–	0	-8	-14	-12	26

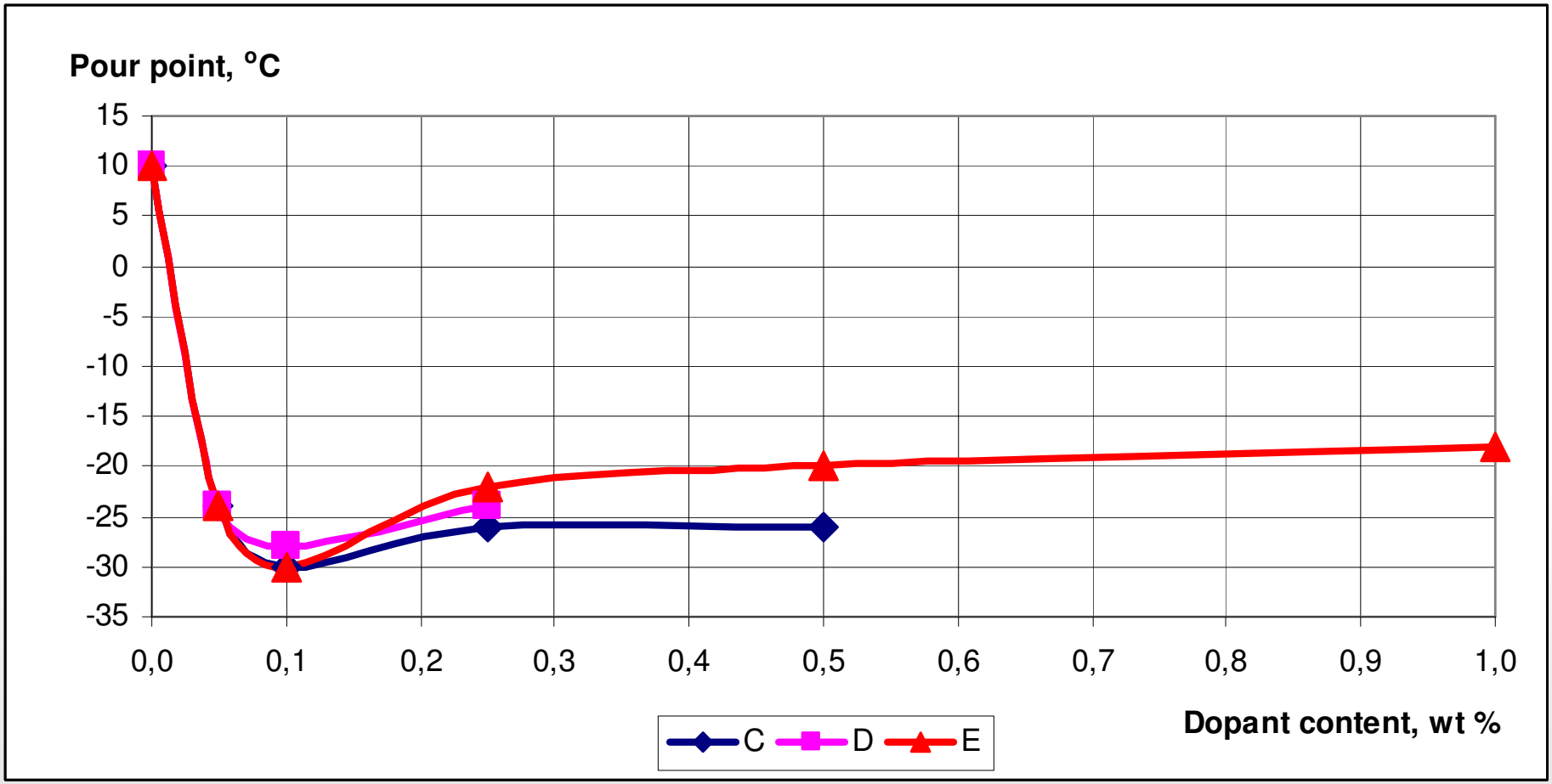


Fig. 14. Dependence of pour point of coker KGO fraction on content of dopant C, D and E

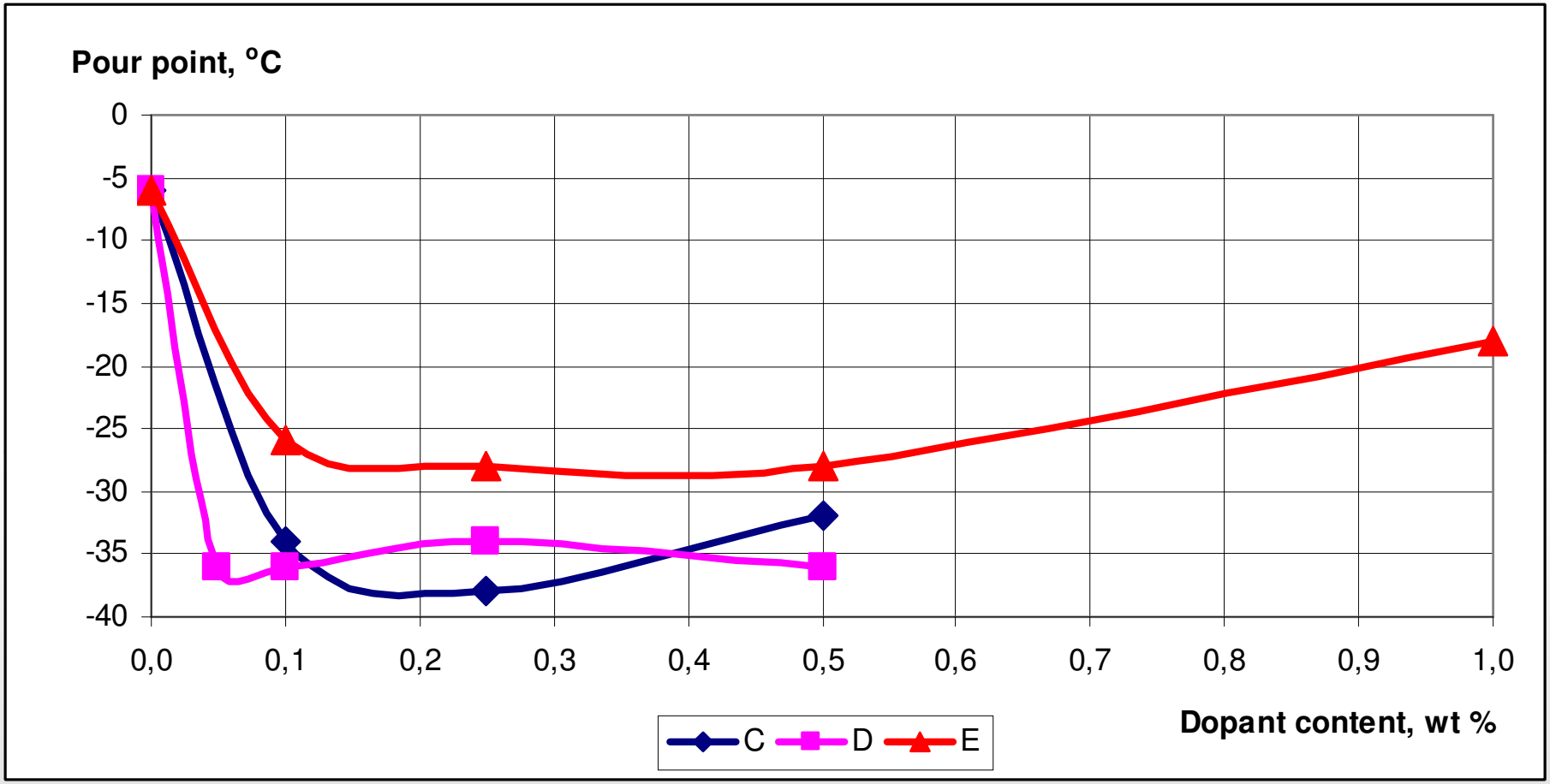


Fig. 15. Dependence of pour point of catalytic KGO fraction on content of dopant C, D and E

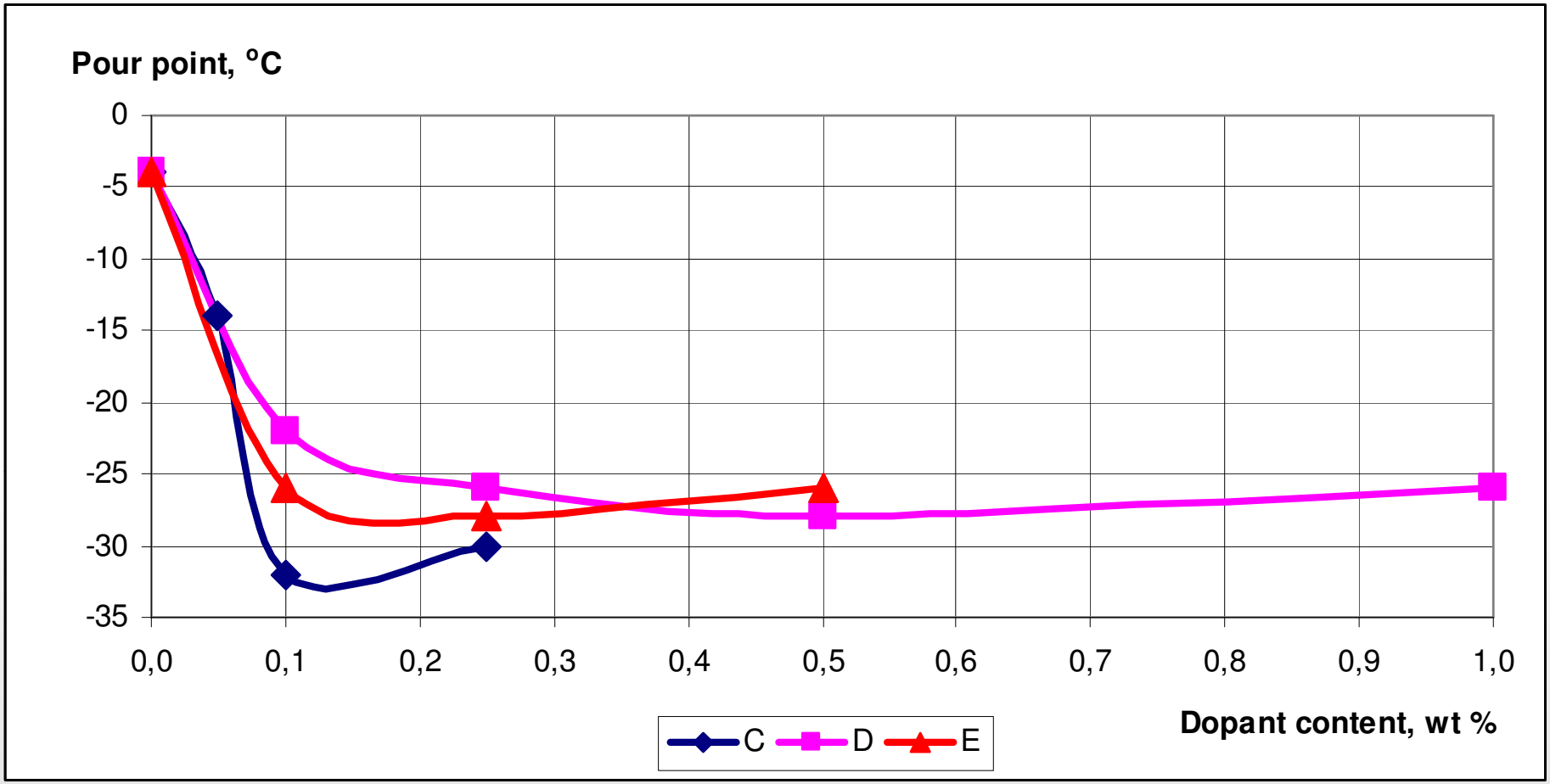


Fig. 16. Dependence of pour point of extract of the 275-400°C fraction on content of dopant C, D and E

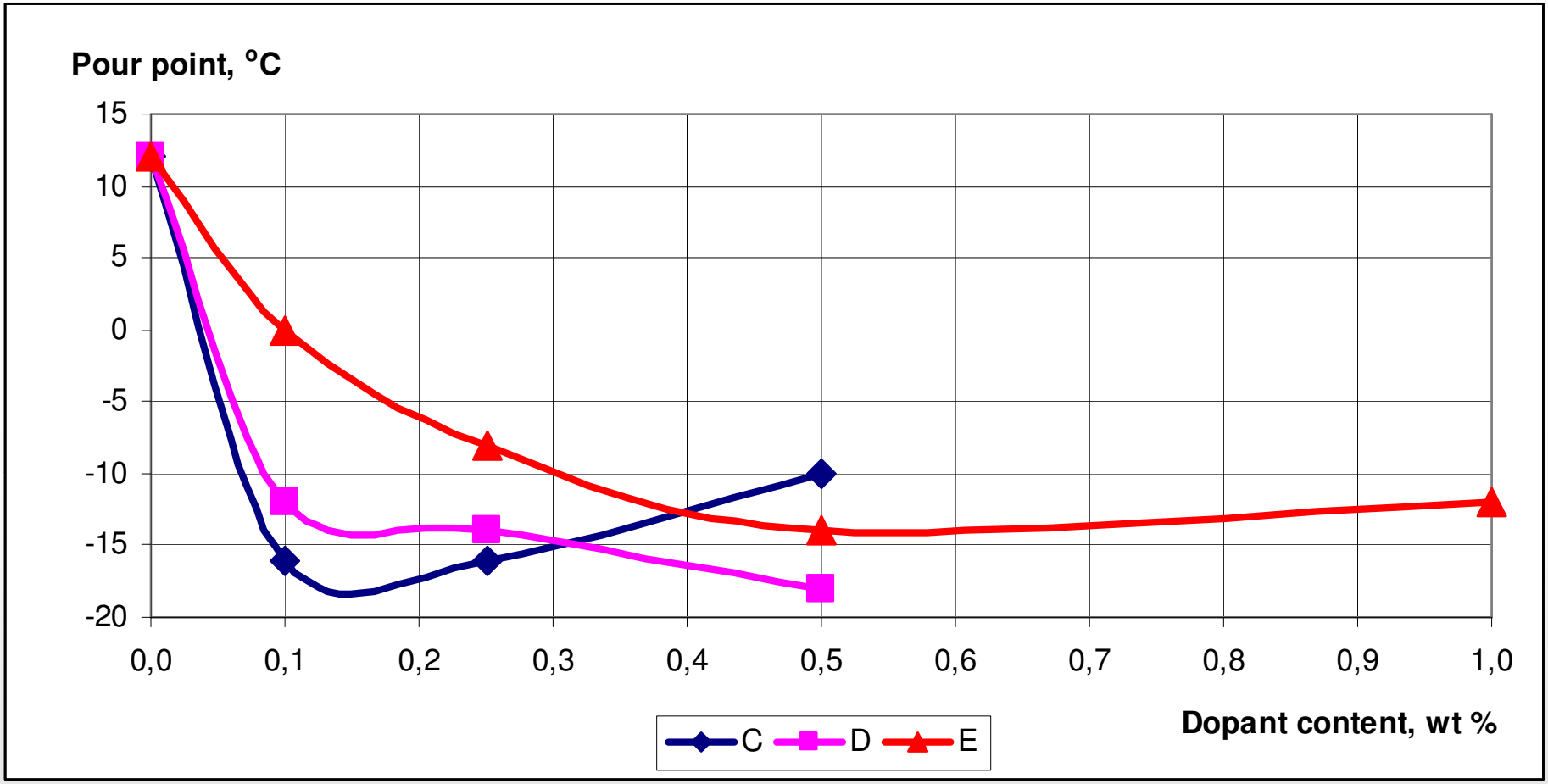


Fig. 17. Dependence of pour point of straight-run distillate fraction 275-400°C on content of dopant C, D and E

All of the test depressants reduced the pour-point of both the initial fraction and the extract by 20-30^{o}C: from +12 to –(8-16)^{o}C for the 275-400^{o}C stright-run distillate and from -4^{o}C to –(22-32)^{o}C for the extract at a concentration of set I additives A-E of 0.10-0.25 wt % and set II additives F-J of 0.25-0.50 wt %.

The maximum depression in both cases reached 24-28^{o}C for additives A-E and 26-42^{o}C for additives F-J;

Conclusions

1. The most effect have additives of ethylene-vinyl acetate copolymers with a VA content of 30-40 wt % and with MFI of 0.7-19.2;

2. The highest depressant ability for the vacuum gas oil fractions are displayed by samples C, D and E. The highest susceptibility to pour-point depressants is exhibited by the vacuum gas oil fraction of 350-540°C, which produces the maximal depression of 36°C;

3. Additives G, H and I having MFI values of 0.7, 19.2 and 40.0, respectively, exibit the highest depressant ability. In this case, the vacuum gas oil fraction of 350-540°C displays the highest susceptibility to these depressants: the maximum pour-point depression for this fraction is 32°C. Of the vacuum gas oil fractions examined, the 350-540°C fraction having a solid paraffin content of 6.08% and a melting point of 57°C exhibits the best susceptibility.

4. When set I depressants with different amounts of VA units are added to the straight-run diesel fraction, the greatest depressing effect is achieved with additives D (VA=35.4 wt %) and E (VA=40.4 wt %), which lower the pour-point of the fraction to -34°C at an optimal concentration (0.5 wt %). In the case of set II additives with different melt flow indices, the greatest depressant effect was obtained with additive I (MFI=40.0) at its concentration of 0.25-0.50 wt %;

Conclusions

5. The coker gas oil and catalytic gas oil fractions exhibit good susceptibility to the test depressants, the maximum pour-point depression is 30-40°C (40°C for the coker gas oil and 32°C for the catalytic gas oil) at an additive concentration of 0.1 wt %. The pour point of the coker gas oil was decreased from +10 to -30°C and that of the catalytic gas oil decreased from -6 to -36°C;

6. All of the test depressants reduced the pour-point of both the initial fraction and the extract by 20-30°C: from +12 to –(8-16)°C for the 275-400°C stright-run distillate and from -4°C to –(22-32)°C for the extract at a concentration of set I additives A-E of 0.10-0.25 wt % and set II additives F-J of 0.25-0.50 wt %. The maximum depression in both cases reached 24-28°C for additives A-E and 26-42°C for additives F-J;

7. All of the test fraction have good susceptibility to EVAC additives: depending on the fractional and hydrocarbon group compositions of the fractions, the decrement in their pour-point is as large as 20-40°C on average at an additive concentration of 0.1-0.5 wt %;

Thank you for attention!



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PhD, professor

Head of the Department of Chemical Engineering and Energy Carriers Processing

National Mineral Resources University, St. Petersburg, Russian Federation